The extensive mercury contamination in soil and legacy sediments of the Paglia River basin (Tuscany, Italy): interplay between Hg-mining

(Article begins on next page)

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Corresponding Author:	SILVIA FORNASARO Università degli Studi di Firenze Florence, Toscana ITALY
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Università degli Studi di Firenze
Corresponding Author's Secondary Institution:	
First Author:	SILVIA FORNASARO
First Author Secondary Information:	
Order of Authors:	SILVIA FORNASARO
	Guia Morelli
	Valentina Rimondi
	Cesare Fagotti
	Rossella Friani
	Pierfranco Lattanzi
	Pilario Costagliola
Order of Authors Secondary Information:	
Funding Information:	
Abstract:	Purpose The extensive Hg contamination in soil and sediments occurring along the Paglia River (Central Italy) is the result of the interplay between the geomorphological changes of the river and the anthropic activities, primarily associated to the exploitation of Hg-deposits in the Monte Amiata mining district (MAMD). The present study points out the implications of the morphological changes occurred in the last 200 years of the Paglia River on the distribution of Hg along the floodplain and riverbed, which today represent one of the main Hg-reservoirs in the MAMD. Materials and Methods The temporal changes of the Paglia riverbed and the extent of its alluvial deposits were reconstructed by a GIS-based analysis of the available maps and aerial photos. The Hg-concentration in soil and sediment samples, collected along five transects transverse to the Paglia River course, was determined by ICP-MS. Results and Discussion Samples along the investigated Paglia River segment typically show Hg-contents exceeding the Italian threshold for residential and public green soil use (1 mg kg $^{-1}$). The distribution of Hg in the Paglia floodplain results from the combination of exceedance of sediment yield to the river during mining activities, that fed the floodplain with large amounts of Hg-contaminated sediments during its braided stage

	about 100 years ago, and the morphological changes of the river, that led to the evolution from a braided to the present-day single channel river. The magnitude of the extension of Hg-contamination, the river geomorphologic changes, and the processes of transport, deposition, and re-suspension did not allow a natural "clean up" of the river system, which shows a low resilience. Under high flow conditions, and especially in coincidence with intense rain events, large amounts of Hg stored in the overbank sediments are mobilized and redistributed, contributing to make the floodplain a secondary Hg-source. Extreme weather events, expected to intensify as a consequence of climate change, will contribute to the recurrent distribution of Hg-contaminated legacy sediments in the floodplain and along the Paglia river course. Conclusion From a water/land management perspective, the variability of the river flow, associated with an increase of extreme flood events driven by climate change, will affect the distribution of Hg-contaminated particles in the Paglia River, contributing to the Hg input into the Mediterranean Sea in the future.
Response to Reviewers:	Comments from the Editor Paglia River always with capital letter R The text was modified according to the suggestion of the Editor. Paglia River and Tibera River should be preferred to Paglia R. and Tibera R. The text was modified according to the suggestion of the Editor. "overbanks" should be written as "overbank sediments" The term was modified where deemed necessary. units should be written with powers in superscript, e.g., mg kg-1 (with -1 as superscript), not mg/kg The text and the figures were modified according to the suggestion of the Editor. "braidplain" should be considered instead of floodplain, where the term is more appropriate e.g., in Fig. 2 We believe it is more appropriate to keep the generic term "floodplain", because in the study area the suggested "braidplain" would be applicable only in the pre-mining period. Reviewer #1 While I do not have a background in river morphology, I found the paper compelling and well written. I support its publication. My one critique it that while the title has "climate change" in it, and the body of the paper and the conclusion discuss climate change, the theme does not show up in the abstract section. This problem needs to be addressed. As suggested by the reviewer, we emphasized in the abstract the hypothesized relation to climate change (lines 33-35). Moreover, we added a statement at the end of the Introduction (lines 83-84) Reviewer #2 This paper entitled "The extensive mercury contamination in soil and legacy sediments of the Paglia River basin (Tuscany, Italy): interplay between Hg-mining waste discharge along rivers, 1960s economic boom, and ongoing climate change" represents interesting study on temporal changes in contamination of floodplain soils and sediments in former mining watershed. It brings new insight onto the interplay between mine production/economical situation, river stages and climatic variables. But major revisions of certain sections are needed so that this paper has context for an international reader and complies with international standards. Apart of the minor issues listed below, I have serious problem with the section 2.4 Geochemical analysis. This section should be expanded and described in much greater detail. What exactly means that "concentrations were recalculated to the grain size fraction >2 mm" and why was this done? This should be explained for reader. We are aware that this point of recalculation is a (probably useless) complication. However, it is a specific requirement of the Italian legislation (DL 152, 2006 "Norme in materia ambientale"), and as such cannot be ignored by environmental agencies. As stated in the Acknowledgments, the study arises from an agreement between the University and the regional environmental agency (ARPAT) and it was ultimately funded by the regional government. In practice, according to the Italian legislation

requirement, the concentration of a given pollutant, actually measured in the fraction <2 mm, has to be normalized to the total weight of the sample (including the fraction >2mm). This requirement is based on the assumption that the fraction > 2mm does not contain significant amounts of the pollutant, an assumption that may be unjustified in some cases, but, as demonstrated in a previous study (Colica et al., 2019), is essentially correct for Hg in the Paglia River sediments. Moreover, in samples collected for this study the fraction >2mm is virtually absent. In conclusion, in this specific case the observance of law requirements does not change the results. We added a phrase in the text stating that the >2mm correction is negligible (lines 192-194)

Furthermore, leaching experiments - why did you do those? I could not find result/comment or discussion on these analyses. Where are these results evaluated? The only place where they can be found is Table 2. I also have some doubts on leaching experiments e.g., what kind of Hg do you think has been mobilized from the sediment by distilled water? Was the eluate filtered? Were selected samples replicated to have an idea about the replicability of leaching? Why are the results of leaching in ug/L (Tab. 2)? This should be recalculated onto solid phase… so that it is directly comparable to the total Hg.
Once and again, the methodology described for the leaching experiments is a law requirement. Indeed, previous studies (e.g., Rimondi et al., Chem. Geol. 380, 2014) suggest that most Hg in this kind of samples occur as extremely low solubility phases (sulfides), so leaching tests with pure water can only remove minimal amounts of (sparingly) soluble phases (e.g., Hg°). The ug/l unit is again according to the law; it can be easily recalculated onto the solid mass. But, overall, we agree with you that these data are of little significance for the paper. Therefore, we removed any mention of these data

Same issue, for the total analysis in the digests - was the repeatability tested? Accuracy was tested by independent standards what are these? Do you mean reference materials (CRM)? If you do, specify which exactly did you use, how many replicates did you make and how precise was the analysis.
At last, you indicate 10% analytical precision - this is rather high. EPA standards for Hg analysis usually aim to 5%? Please comment on this.
Thank you for raising this issue and helping us to clarify this point. We expanded the related paragraphs (lines 192 and following), hopefully answering to your questions. Concerning analytical precision, we point out (as stated in lines 201-203) that we refer to the difference between analyses of different aliquots of the same bulk sample. Precision is usually better than 10%, but in few cases (probably because of the well-known “nugget effect”) is up to 10%. In any case, we believe it does not affect the overall significance of the obtained data.

Please consider moving Table 2 into supplement after editing it with respect to my previous remark. The new Hg data are included in figs 4 and 5. Furthermore Table 2 is only referenced once through the whole paper, but it is quite extensive.
We accepted the suggestion

Figure captions in the Figures section of PDF appear on different pages with different figures… e.g., page 27 and 29, make sure these appear where they should as it complicates work with PDF.
Thanks for the comment. During the resubmission process, we will pay attention to the correct layout of the PDF.

Line 96 m asl - please unify this abbreviation so it is consistent through the whole paper as "m a.s.l."
The text was modified according to the suggestion

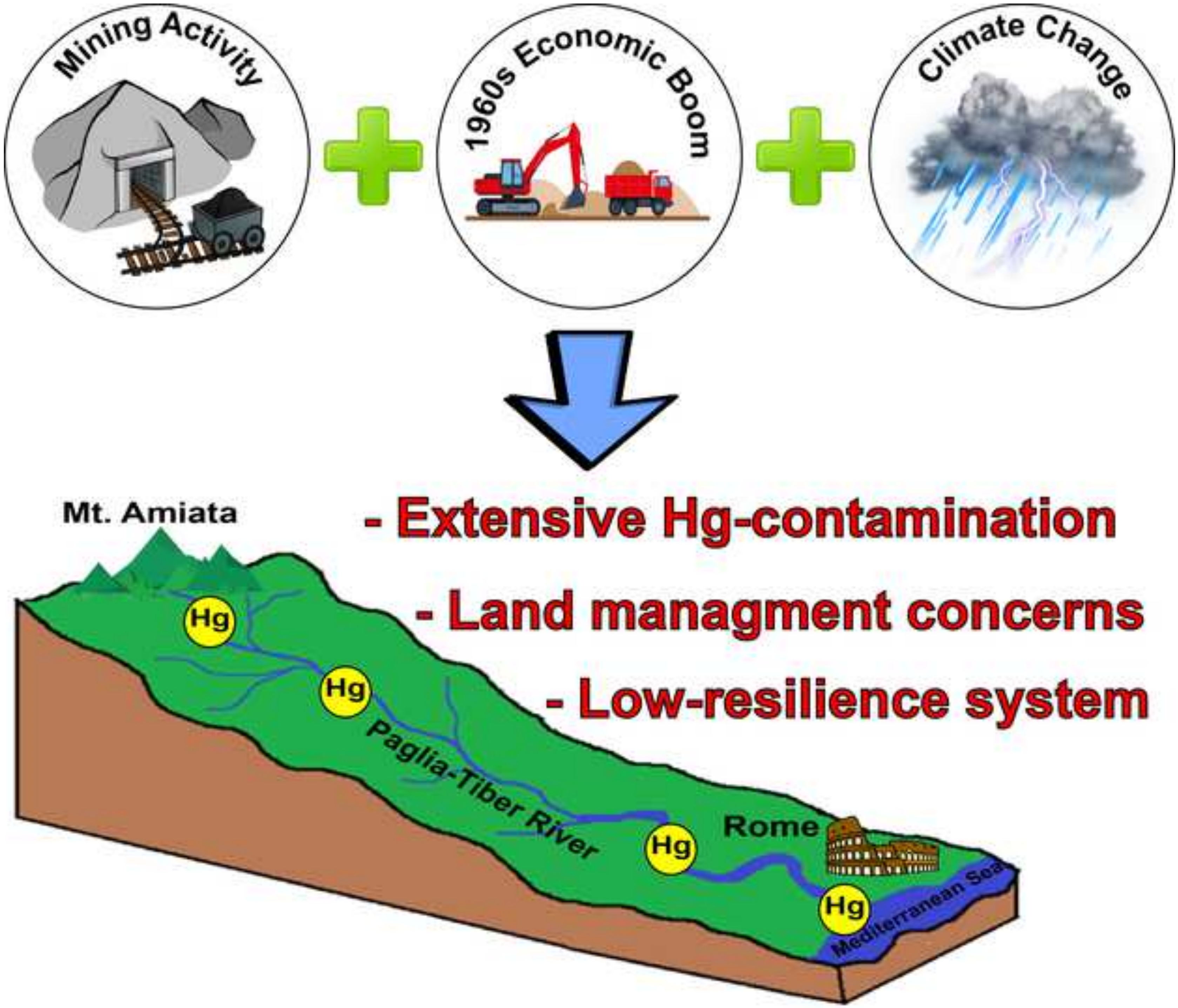
Line 119 what exactly does variable flow mean? Please explain to reader.
We added new information in order to clarify the concept.

Line 256 Thanks for the paragraph above. Very interesting. I wish you indicate at the end when exactly was the complete halt - which year or years.
We added specific details in the text (line 270)

Line 271 channel reduction… was this natural or anthropogenic process?

	As explained in the following lines 287-288, the channel reduction was mainly due to anthropogenic processes (e.g., recovery of land for agriculture, river management works, land-use changes, building of weirs and dams, quarrying of sediments). Line 280 which Italian rivers are we talking about here, be particular We added new information in the text (lines 294-295) Line 282 through the whole paper "World War I" and "World War II" are referred to this way. The text was modified according to the suggestion Line 287-288 I do not understand this sentence. How does can be "contaminated sedimentary bodies suspended"? Please rewrite. We rewrote the sentence. Line 293-294 I do not understand this sentence, especially the end of it about floodplain of 1954. We rewrote the sentence. Line 299-300 Great! We have seen a lot of that here. Thank you for the comment Line 375-376 contraction of snow periods of snow affect river dynamics but how? The reader should be informed. The sentence was removed. Line 382 Good. I acknowledge these statements on conservation measures. Thank you for the comment.

Graphical Abstract



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The extensive mercury contamination in soil and legacy sediments of the Paglia River basin (Tuscany, Italy): interplay between Hg-mining waste discharge along rivers, 1960s economic boom, and ongoing climate change

S. Fornasaro[1*], G. Morelli[2], V. Rimondi[1], C. Fagotti[3], R. Friani[3], P. Lattanzi[2], P. Costagliola[1]
1. Dipartimento Scienze della Terra, Università di Firenze, Via G. La Pira, 4, 50121 Firenze, Italy
2. CNR-Istituto di Geoscienze e Georisorse, Via G. La Pira, 4, 50121 Firenze, Italy
3. ARPA Toscana, Area Vasta Sud, Loc. Ruffolo, 53100 Siena, Italy
*Corresponding author: silvia.fornasaro@unifi.it

Abstract

Purpose

The extensive Hg contamination in soil and sediments occurring along the Paglia River (Central Italy) is the result of the interplay between the geomorphological changes of the river and the anthropic activities, primarily associated to the exploitation of Hg-deposits in the Monte Amiata mining district (MAMD). The present study points out the implications of the morphological changes occurred in the last 200 years of the Paglia River on the distribution of Hg along the floodplain and riverbed, which today represent one of the main Hg-reservoirs in the MAMD.

Materials and Methods

The temporal changes of the Paglia riverbed and the extent of its alluvial deposits were reconstructed by a GIS-based analysis of the available maps and aerial photos. The Hg-concentration in soil and sediment samples, collected along five transects transverse to the Paglia River course, was determined by ICP-MS.

Results and Discussion

Samples along the investigated Paglia River segment typically show Hg-contents exceeding the Italian threshold for residential and public green soil use (1 mg kg^{-1}).

The distribution of Hg in the Paglia floodplain results from the combination of exceedance of sediment yield to the river during mining activities, that fed the floodplain with large amounts of Hg-contaminated sediments during its braided stage about 100 years ago, and the morphological changes of the river, that led to the evolution from a braided to the present-day single channel river.

The magnitude of the extension of Hg-contamination, the river geomorphologic changes, and the processes of transport, deposition, and re-suspension did not allow a natural “clean up” of the river system, which shows a low resilience. Under high flow conditions, and especially in coincidence with intense rain events, large amounts of Hg stored in the overbank sediments are mobilized and redistributed, contributing to make the floodplain a secondary Hg-source. Extreme weather events, expected to intensify as a consequence of climate change, will contribute to the recurrent distribution of Hg-contaminated legacy sediments in the floodplain and along the Paglia river course.

Conclusion

From a water/land management perspective, the variability of the river flow, associated with an increase of extreme flood events driven by climate change, will affect the distribution of Hg-contaminated particles in the Paglia River, contributing to the Hg input into the Mediterranean Sea in the future.

Keywords
legacy sediments; fluvial dynamics; mercury; Monte Amiata

1. Introduction

Geomorphic features of riverine systems result from the balance of many parameters (e.g., water and total sediment load; Schumm and Harvey 1999; Calle et al. 2017), that may in turn be affected by factors such as climate changes and human activities (Grabowski and Gurnell 2016; Marchamalo et al. 2016; Calle et al. 2017; Owens 2020; Vauclin et al. 2020). Specifically, in fluvial systems draining mining areas, mining activities may contribute significantly to the modification of river morphology, influencing sediment supply and the associated processes of erosion, transport, and deposition (e.g., Ciszewski and Grygar 2016; Davis et al. 2018). In addition, pollutants associated with mining particulate, such as heavy metals, are responsible of large-scale contamination up to several hundred kilometers away from the mining area (Martin and Maybeck 1979; Schafer et al. 2006; Mayes et al. 2013; Rimondi et al. 2019). Mining-contaminated legacy sediments deposited along waterways may remain stored within river channels and on floodplains for hundreds or thousands of years (Salomons and Förstner 1984; Macklin and Lewin 1989; Pavlowsky et al. 2017; Davis et al. 2018; Rimondi et al. 2019). They become diffuse sources of contamination if re-mobilized, for example by overbank erosion during flood events, or by human activities (e.g., gravel mining; Macklin et al. 1997; Pavlowsky et al. 2017; Colica et al. 2019). Floodplains therefore play an important role as both sinks and sources of metal contaminants in mined watersheds (Bradley 1989; Horowitz 1991; Lecce and Pavlowsky 1997; Coulthard and Macklin 2003; Ciszewski and Grygar 2016; Pavlowsky et al. 2017).

In the last 200 years, Italian waterways experienced considerable changes that triggered deep modifications of their original morphology (Surian and Rinaldi 2003; Cencetti et al. 2017, and references therein), similarly to other European rivers (e.g., Garcia-Ruiz et al. 2011; Debolini et al. 2015; Pavanelli et al. 2019). Incision and narrowing of the active channel were the most frequently observed modifications (Cencetti et al. 2017). The Tiber River (central Italy) and its tributary Paglia River are no exception and were affected by similar processes. The Paglia River (49 km length) is one of the right-side tributaries of the Tiber River. Its morphological changes play a key role for the delivery of Hg to the Mediterranean Sea, since the river directly collects the runoff from one of the largest Hg ore districts in the world, the Monte Amiata Mining District (MAMD). Previous works described the morphological changes occurred in different sections of the Paglia River (e.g., Cencetti et al. 2017), and the pervasive distribution of Hg in river sediments and soils of the Paglia River floodplain, highlighting how fluvial dynamics contribute to transport Hg contaminated sediments up to 200 km downstream the MAMD (Colica et al. 2019; Rimondi et al. 2019).

The present study points out the implications of the morphological changes in the last 200 years of the Paglia River (Tuscan stretch) on the buildup of the fluvial overbanks, which today represent one of the main Hg reservoirs in the MAMD district. Geochemical data obtained during a sampling campaign conducted in 2020 by the Regional Environmental Protection Agency of the Tuscany (ARPAT) and by the environmental mineralogy group at Dipartimento di Scienze della Terra (DST), Università di Firenze, complement previous

studies by Colica et al. (2019) and Rimondi et al. (2019). These new results were integrated with previous data to assess the spatial and temporal variability of Hg contamination in the Paglia River floodplain.
Specifically, the aims of this study are: i) to understand how the geomorphological (natural and anthropogenic) changes control the Hg distribution in the Paglia River floodplain; ii) to verify the implications of flood events on Hg distribution and resilience of the river system, taking into account the potential consequences of climate changes.

2. Materials and methods

2.1 *Study area*

2.1.1 Tiber-Paglia River system

The Tiber River is the third longest river in Italy, flowing through the city of Rome and into the Mediterranean Sea (Cattuto et al. 1988; Ciccacci et al. 1988; Fredduzzi et al. 2007; Cencetti et al. 2017). The adjustments in its course in the last 250 ky were caused by an interplay between glacio-eustasy, sedimentary processes and regional uplifts (Marra et al. 2019). It was subjected to anthropic pressure probably before the establishment of the Roman Empire (Salomon et al. 2017). The most evident modifications took place during the 20th century and in the last decades following the Italian economic expansion, peaked between 1950 and 1970, with the construction of dams, sediment mining, and changes in the agriculture practices. The morphological changes occurred in the Tiber River are like those observed elsewhere in the Apennine area (Cencetti and Tacconi 2005; Rinaldi and Simon 1998; Surian and Rinaldi 2003).
The Paglia River is one of the right-side tributaries of the Tiber River and arises from the junction of Pagliola an Cacarello creeks (388 m a.s.l., Fig. 1). The former drains the main mining and metallurgical center of MAMD near the Abbadia San Salvatore township. The Paglia River starts its course southeastward along a gentle slope, reaches the border between Tuscan and Latium regions (266 m a.s.l.) about 15 km from the starting point, and it enters into the Tiber River south of the city of Orvieto (Fig. 1C).
The geological-geomorphological structure of the upper basin of the Paglia River is linked to the formation of the Apennines during the Tertiary, and the subsequent post-collisional events (Marroni et al. 2015). The geology of the basin from the base to the top includes (Fig. 1C; Marroni et al. 2015): i) Tuscan and Ligurian Units (Paleozoic – Lower Miocene); ii) marine, transitional, and continental sedimentary successions (Lower Pliocene – Quaternary); iii) volcanic and volcano-sedimentary successions (Upper Pliocene – Upper Pleistocene); iv) continental deposits-debris and alluvial deposit (Quaternary). The quaternary continental deposits are characterized by i) holocenic fluvial deposits, present along the Paglia River valleys and its main tributaries, consisting mainly of sandy-silty beds and pebbles. The Paglia River cuts through its alluvial deposits, locally forming various orders of terraces; ii) Pleistocene deposits: fluvial-lacustrine deposits, mainly formed by conglomerates with sandy-silty beds levels. These deposits are arranged on large terraces located at higher elevation (from 5 to 20 m) compared to the current course of the Paglia River (e.g., Colica et al. 2019). The presence of substrates characterized by erodible lithologies (Mio-Pliocene deposits) contributed to erosion processes with the formation of peculiar morphologies such as the "*biancane*" and the “*calanchi*” (Ciccacci et al. 2009). The shape of the Paglia River basin and the trend of the hydrographic network are

closely correlated with the structural characteristics of the Radicofani and Cetona grabens, set on normal fault systems with NNW-SSE trend, and trend-transforming systems with WSW-ENE trend (Sani et al. 2016).
This area is characterized by a Mediterranean temperate climate, with hot and dry summer and cold and rainy winter. The average annual temperature is 10.5°C (period 1953 – 2000), and the average annual precipitation is 1480 mm (over the period 1925 – 2000; Ciccacci et al. 2009). About ⅔ of the total annual precipitation is concentrated in the autumn-winter season (Ciccacci et al. 1988). The Paglia River flow regime is controlled by seasonal variability, ranging from 0.3 m^3 s^{-1} to 26 m^3 s^{-1} monthly average (Fredduzzi 2005), with an annual average discharge of 2.45 m^3-s^{-1} (Cencetti et al. 2017). The hydrological periods are difficult to define (Moretti et al. 1988), due to the torrential regime of the initial part of the Paglia River, that may rapidly reach very high flow, collecting water contributes of a high number of tributaries. In general, the lowest and the highest water flow levels were recorded at the end of the summer period (September-October) and in winter-spring (November-March; Rimondi et al. 2014), respectively. An increase in mean monthly discharge was observed since 2003, due to a higher frequency of extreme flood events (Pattelli et al. 2014; Rimondi et al. 2014; Cencetti et al. 2017). This trend peaked with the flood of 2012 (mean monthly discharge: 91.7 m^3s^{-1}, peak flow: 2663 m^3 s^{-1}; Cencetti et al. 2017).
The Paglia River is physically shaped by sequential seasonal events of flooding and drying over a yearly cycle (Gasith and Resh 1999), reflecting the highly irregular rainfall patterns, with marked differences between wet and dry seasons, as most Mediterranean rivers. The concomitance of intense rainy days after dry summer periods, coupled with the scarce vegetation in the area, causes flash floods, with associated sliding-like mud and debris flows (Di Tria et al. 1999).

2.1.2 The Monte Amiata mining district (MAMD)

The MAMD district covers an area of ~400 km^2 and includes 42 former mines and 4 Hg roasting plants (Ferrara et al. 1998). The MAMD produced about 102,000 t of Hg between 1860s and 1980s (Colica et al. 2019), representing the third cumulative production ever reached in the world (Rimondi et al. 2015). The on-site metallurgical processing of cinnabar, the principal ore mineral, produced wastes, called calcines, with significant residual Hg contents (25 – 1500 mg kg^{-1}; Rimondi et al. 2012; 2015). These wastes were often abandoned or discharged directly into the rivers adjacent to the mines, or used as filling material for road networks, house foundations, or landfills in crops (unpublished report, item T-1268 of the archives of the exploration company RIMIN). Numerous studies highlighted the environmental impact caused by over a century of mining and metallurgical activities in the MAMD, and the consequent contamination of Hg in the sediments transported by the Paglia River (Rimondi et al. 2019, and references therein). The first studies concerning the dispersion of Hg in the rivers of the MAMD date back to Dall'Aglio (1966) and Dall'Aglio et al. (1966), who detected extensive Hg contamination in stream sediments and waters. Bombace et al. (1973) estimated that at least 165 t of Hg were dispersed in the Paglia River from 1954 to 1963, the main period of mining activity. The same authors found up to 10.5 mg kg^{-1} of Hg in stream sediments in the Paglia River, and up to 71.1 mg kg^{-1} in the Siele creek, a right-side tributary (Fig. 1C). As stressed by Colica et al. (2019), the Paglia River overbank sediments represent a secondary pollution source, containing not less than 63 t of Hg.

2.2 Geomorphological and multi-temporal analysis of channel changes

The temporal changes of the Paglia riverbed and the extent of its alluvial deposits were reconstructed by GIS-based analysis of the available maps and aerial photos from the period of maximum mining production to date. Specifically, we used:

- 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.
- Aerial photos taken in 1954 (IGM, scale 1:33,000), coinciding with the maximum production period of MAMD (Caselli et al. 2007).
- Aerial photos taken in 1978 (IGM, scale 1:33,000), coinciding with the final production period of MAMD.
- Aerial photos from 1988 to 2016 (post-production period, during which partial reclamation of two main mining and smelting centers (Siele and Abbadia S.S.) was undertaken).
- Satellite images from Google Earth in 2019 (current status).

Through the open-source software Qgis 3.16 (Hannover; https://qgis.org/it/site/), the main morphological characters of the riverbed and floodplain were vectorized. The result consists of two vector layers: a linear type, representing the riverbed (dashed lines in the figures); and a polygonal one, corresponding to the floodplain (colored fill in the figures). Areas and widths were calculated by using the QGIS *Calculator Field* tool.

In Table 1 we report the definition of all the geomorphological terms used in the text.

2.3. Soil and stream sediment sampling

The geochemical analyses of soil (n = 74) and stream sediments (n = 17) presented in this study combine data of soil and stream sediment collected along five transects transverse to the Paglia River course (TP1, TP2, TP3, T4, TP5; Fig. 1C). New samples were collected from transects studied in previous works by Colica et al. (2019) (TP2 and TP4) and Rimondi et al. (2019) (TP1 and TP5), in the Tuscan portion of the Paglia River basin (Tab. 2).

A new transect (TP3) was chosen to integrate the previous ones. Stream sediments refer to the active Paglia River main course and were collected in the top layer (top 5-10 cm), below the water surface. Soils were collected about every 2 or 3 meters along the transect in the superficial horizon (0-30 cm) of the floodplain. All samples were collected as composite samples of about 1 kg, made up by mixing five sub-samples taken within a square of 5 m side around the selected sampling point, by using a shovel.

2.4 Geochemical analysis

The ARPAT laboratory (Siena, Italy) carried out sample preparation and chemical analysis of collected sediments and soils. Soils and sediments were homogenized, dried in air, sieved with a 2 mm sieve (as required by Italian national guidelines; D.Lgs. 152/2006), and then pulverized with a rotating ball mortar. Following the same Italian national guidelines, Hg concentrations were determined in the fraction <2mm, and were then recalculated to the whole samples (i.e., including the fraction >2 mm). This procedure is mandatory for Italian environmental agencies; in any case, the fraction >2mm was minimal in all collected samples, therefore the application of this methodology had a negligible effect on the analytical results. Prior to analysis, soil and sediment powders were digested in aqua regia in a microwave oven (U.S. EPA 2007; 2014 methods). Concentrations of Hg were determined by ICP-MS (Inductively Coupled Plasma Mass Spectroscopy; UNI EN 2016). The ARPAT laboratory is subjected to periodical quality checks by an independent organization (Accredia) according to the standard ISO/IEC 17025 and it takes part to the SNPA interlaboratory network for cross-checking. Specifically for Hg analyses, accuracy is determined employing the certified material ERM CC141 (certified Hg content: 0.083 ± 0.017 mg kg^{-1}; average of laboratory analyses: 0.079 ± 0.009 mg kg^{-1}). The overall analytical precision of the method is <10%, as determined by replicate analyses of different aliquots of the same bulk sample.

3. Results

3.1 Geomorphological changes along the first section of the Paglia floodplain

Aerial photos and maps from 1883 to 2019 allowed to reconstruct the temporal changes of the riverbed and the floodplain along all the transects, as shown in Figure 2, whereas changes in land-use and geomorphologic features around each transect are reported in the supplementary material (Fig. S1-S5). In the following, we will analyze the temporal changes of the Paglia River floodplain, with reference to area variations. Changes in the floodplain width measured along transects were also considered; however, local features and/or fluctuations (e.g., due to climate variability) may affect the general processes controlling this parameter.

In the investigated segment of the Paglia River, the main changes observed during the 1883–2019 time frame include anthropogenic intervention and modifications in the principal road network, building of an industrial area that occupies part of the river valley, modifications of crop field extension, and other changes in land use (see supplementary materials for further details).

Figure 3 shows that a reduction of the floodplain area occurred from the end of 1800. The decrease was more pronounced between 1954 and 1978, with a reduction of almost two thirds (about 62%) of the total area (from 2.8 to 0.9 km^2). After 1978, which broadly corresponds to the end of mining activity, the floodplain area was subjected to fluctuations, with a relative increase in the period 1988-1998 followed by a progressive slow decrease lasting about 15 years and concluded in 2010. After this year until today, the area increased. Specifically, in the three years from 2010 to 2013, the floodplain area doubled its extension (Fig. 3).

On the other hand, in the period 1883-2010 the riverbed experienced a distinct narrowing of its width at all the five transects (Fig. 3; Fig. S1-S5), with a marked reduction occurred between 1954 and 1978. In the following period, the riverbed width remained more or less constant in the upper part of the river, from transect TP1 to TP3. On the contrary, in correspondence with transect TP5, we notice a progressive enlargement (47%) since 2000, while after the confluence with the Senna Creek, at transect TP4, the width of the Paglia River increases, especially during or after major flood events (e.g., after the 2012 flood).

3.2 Mercury concentrations in stream sediments and floodplain soils

Stream sediments and soils sampled along the transects in the Paglia River show highly variable Hg contents (from <0.2 mg/kg to 100 mg kg^{-1}). In Figure 4 the spatial distribution of Hg in sediments and soils along each transect is represented in association with their elevation and lithology. The full dataset is reported in Table S1.

The highest concentration of Hg in stream sediments (64 mg kg^{-1}) was recorded at TP1, while in soils (100 mg kg^{-1}) at transect TP5. Elevated Hg concentrations (1.7-6.7 mg kg^{-1}) were also found in fine sediments collected along transect TP5. These sediments were deposited by a flood event in December 2019, which occurred shortly before the sampling campaign (January-February 2020). This event led to the partial flooding of the field on the left side of the Paglia River.

In correspondence of the transects the Paglia River floodplain is almost entirely anomalous in Hg, i.e. with concentrations above the legal limit (1 mg kg^{-1}) defined by the Italian law for soil for residential and green area use (D.Lgs. 152/06), as shown in Figures 2 and 4. The anomaly boundary can be identified with the pre-anthropic fluvial terraces dated to the Pleistocene (Colica et al. 2019). These Pleistocene terraces are located at higher topographic levels with respect to more recent terraces formed during periods of anthropic activity (Colica et al. 2019). Nevertheless, Hg anomalies (> 1 mg kg^{-1}) are exceptionally found at high topographic altitude and, in some instances, over the Pleistocene terraces (e.g., in the transects TP4 and TP5), typically nearby roads and houses (Fig. 4).

4. Discussion

4.1 Geomorphological river changes: anthropogenic and natural control and impact on Hg distribution in the floodplain

Braided rivers reflect the ongoing adjustment to fluctuating flow and sediment yield, under high sediment delivery conditions coupled with lower sediment throughput, due to a gentle slope (Piegay et al. 2006). Before the mid-1950s, the Paglia River was characterized by several anastomosing channels, river bars and islands, extending over a large area, as observed in the 1883 maps (Fig. S6; cf. Cencetti et al. 2017). This braided stage of the Paglia River coincided with the period during which Hg production, and thus waste production, at MAMD reached its maximum. Conceivably, sediments delivered by MAMD mining and metallurgical activities played an important role in shaping the changes of the Paglia River floodplain. Local miners report that, throughout the mine activity, mining and metallurgical wastes were discharged along the local waterways during rainy periods, and eventually were collected by the Paglia River. Consequently, peaks of Hg production significantly impacted sediment yields in the Paglia River. One of the main production peaks occurred during the first decades of 1900, driven by the increasing demand of Hg fulminate employed during the World War I. As reported by Caselli et al. (2007), during this period the MAMD overcame Almadén in Hg flask trading. After the economic crisis in 1930, production decreased, and maintained low during the World War II, since the district was heavily bombed. After the war, the Hg market, and thus MAMD, had a new important pulse due to the Korean war (Caselli et al. 2007), up to the mid-1960s; in the 1970s the Hg demand began a constant decrease down to a complete halt, with the consequent closure of the mines and plant production site in 1982. The actual mass of the mine wastes produced can be roughly estimated from the total amount of Hg produced (102,000 tons), by the average Hg content of the *tout-venant* (generally less than 1 wt. %; Strappa 1977), and by the metallurgical recovery rate (about 80%; Benvenuti and Costagliola 2016). Based on this scenario, about $12*10^6$ tons of mining/metallurgical wastes may have been produced in the MAMD, corresponding to $6*10^6$ m^3

of sediments (average density: 2 t m^{-3}), the same order of magnitude of the sediment volume presently stored in the fluvial terraces of this waterway (cf. Colica et al. 2019). These estimates suggest that during its braided stage, in the northern stretch of the Paglia River the sediment input was probably high, and significantly contributing to consolidate the braided stage of the river for the first half of 1900s.

In the 1954-1978 timespan, the Paglia floodplain area dramatically shrunk, dropping from 2.6 km^2 to less than 1 km^2 (Fig. 3). The following change to a single channel led to a significant reduction of the floodplain area and produced a local incision of its original valley, leaving most Hg contaminated sediments in its terraces, located at a higher level with respect to the present-day watercourse.

The decrease of the Paglia River floodplain extension was one of the most intense ever recorded compared to floodplain reduction occurred in other Italian rivers (see "phase II" described by Surian et al. 2009). The Paglia River underwent an average reduction of the channel width of about 64% from 1883 to 1954, followed by a further reduction of about 70% from 1954 to 2012. As a result of floodplain narrowing, the Paglia River changed from a pre-1950 braided morphology to the present day wandering single-channel river with low sinuosity (Fig. 2; Fig. S1-S6).

Our study is consistent with the scenario depicted by Cencetti et al. (2017) in the southern stretch of the Paglia River from the Tuscan/Latium border to Orvieto (Fig. 1B), where incision of the Paglia riverbed was enhanced by the erosion of the old floodplain consequent to the increase of gravel mining into the riverbed and recovery of land for agriculture, which reduced supplies of sediment and caused a deficit in sediment transport (Cencetti et al. 2017; Colica et al. 2019). The tendency to riverbed incision is actually a common phenomenon observed in the same period in many other Italian and Mediterranean rivers (e.g., Brenta, Piave, Cellina, Tagliamento, and Torre Rivers in Italy; and Rambla de la Viuda in Spain), mainly steered by gravel mining (Surian and Rinaldi 2003; Aringoli et al. 2015; Cencetti et al. 2017; Calle et al. 2017; Dang et al. 2014). Gravel mining was intense in Italy starting from 1950s up to 1980s (Surian et al. 2009), driven by the post II World War II economic expansion, and impacted river hydromorphologies, leading to scarcity of sediments, unbalanced river systems and modification of the long-term river morphodynamics, long after cessation of gravel mining of the riverbed (e.g., Calle et al. 2017).

The change from a braided to a single channel river had a profound consequence on the distribution of Hg contamination in the Paglia River basin. Due to the gradual deepening and narrowing of this single fluvial channel, Hg-contaminated sediments were deposited at higher topographically levels than the channel itself. One of the main consequences of this process led to a change in the transport/deposition cycle and to a tendential loss of mobility of the material deposited on the overbanks. Therefore, nowadays Paglia River contaminated sediments in the overbanks are no longer reached by the water flowing along the river channel, except during flood events. The extent of the overbank deposits impacted by Hg pollution, broadly corresponds to the floodplain built up by the river during the past century. More precisely, along the examined transects, the extension of Hg contaminated sediments roughly coincides with the 1954 floodplain.

Additionally, anthropogenic intervention may have contributed and still contributes to the unusual Hg contamination (Hg ≥ 1 mg kg^{-1}; D.Lgs. 152/2006) in areas not subjected to the direct influence of the Paglia River and its tributaries, i.e., at higher elevations than those reached by the Paglia River during floods, and at a higher elevation than the terraces formed in the last century. This is observed almost systematically where

transects intercept streets or houses, such as near transects TP1 and TP5. Construction works such as road embankments or foundations of houses may indeed contain anomalously high values of Hg, because between 1954 and 1978 it was common practice the use of mining and metallurgical waste as building material.
Another contribution to the dispersion of Hg can be ascribed to the indirect effect of agricultural practices (soil amendments, irrigation, or artificial drainage), that may have caused the rearrangement and redistribution of superficial soil layers and associated Hg in fields located in the alluvial floodplain (e.g., Montagne et al. 2009).
In summary, our study indicates that the effectiveness with which Hg-contaminated sediments were entrapped/stored along the Paglia River is probably the result of an incidental interplay between i) Hg mining, that fed the Paglia River floodplain with large amounts of Hg-contaminated sediments during its braided stage, and ii) the economic expansion of Italy after the World War II and the subsequent changes of the morphological features of Paglia River (due to gravel mining and other anthropogenic modifications), that enhanced the change to a single channel morphology of the Paglia River.

4.2 Implications of flood events on Hg distribution and resilience of the river system

Local river morphology, sediment input and runoff, land uses and climate variability control fluvial dynamics (Schumm and Harvey 1999; Grabowski and Gurnell 2016, Marchamalo et al. 2016; Calle et al. 2017; Owens 2020). After the closure of Hg mining, the spatial pattern of Hg downstream the Paglia River became a function of floods and high-water events rather than of Hg released to the river from mining activity (dashed black areas in Fig. 2). In the last 10 years, flood events occurred along the Paglia River caused the erosion of part of the previously built river terraces (Pattelli et al, 2014; Cencetti et al. 2017; Colica et al. 2019). During the 2012 flood, in the lower section of the Paglia River (after the Siele creek confluence), the riverbed temporarily occupied part of the 1954 floodplain, reactivating several bars (as for example at TP5, Fig. S5). The incremented high erosion capacity caused an enlargement of the local river channel. Additional examples of the substantial changes on the width of the riverbed were observed after a flood event in December 2019, when the collapse of the riverbanks and part of the Cassia Road, about 3 km upstream of the TP2 transect, occurred.
The impact of floods on river morphology in the northern segment, highlighted in Figure 3, led to the increase of the Paglia floodplain area after the 2010 flood. A similar phenomenon was observed by Cencetti et al. (2017) in the southern stretch of the river, emphasizing that floods may partially restore the Paglia riverbed extension. These authors observed that by reactivating sediment supply, floods may restabilize channel morphology to near-reference conditions (i.e., pre-1954, pre-single channel), adjusting fluvial landforms as a response to the new hydrodynamic conditions (Simon 1989; Simon and Rinaldi 2006; Calle et al. 2017). Floods indeed play a crucial role in reshaping the patterns of pollutants dispersal, eroding, and transporting contaminants temporarily stored in channel and on overbanks to the floodplain (Coynel et al. 2007; Novakova et al. 2015; Ciszewski and Grygar 2016; Ponting et al. 2020). In river systems draining mining areas, storm and flood events have a significant control on the episodic transport of contaminants, and the impacts have been described in other Hg mining districts (e.g., Širca et al. 1999; Whyte et al. 2000; Springborn et al. 2011; Singer et al. 2013; McKee et al. 2017). During floods, enormous quantities of Hg-contaminated particulate are

mobilized because of higher runoff and the increased capacity of the stream to erode riverbanks. Following erosion, Hg transported as particulate suspended matter may increase up to 80-fold (Whyte et al. 2000).

In the Paglia River, a distinct increase in Hg content was recorded immediately after the 2012 flood in stream sediments collected around transect TP1, with up to 905 mg kg^{-1} of Hg, with respect to pre-flood values of 14 mg kg^{-1} (Pattelli et al. 2014). Similarly, after a flood event in 2019, mud deposited in the fields close to transects TP5 and TP1 was characterized by Hg content up to 6.7 mg kg^{-1} and 34 mg kg^{-1} respectively (Fig. 2A and E, dotted areas). This recurrent phenomenon is highlighted in Fig. 5, showing that high Hg pulses in stream sediments are recorded during or shortly after floods along the northern stretch of the Paglia River.

Figure 5 shows, in addition, that a marked increase in Hg in stream sediments is observed in connection with the main flood events occurred since 2010. On the other hand, in the last years a decrease of Hg concentration has not occurred with increasing distance from the mine site of Abbadia San Salvatore, as could be expected by a "natural clean up" of the system.

Under normal water flow conditions, Hg associated to the Paglia stream sediments is progressively washed away or diluted by a solid load that is not anomalous in Hg. The shifts between normal flow and flood events enhance the erosion of Hg-rich old (syn-mining) terraces, representing the actual overbanks in some part of the river, causing an alternance of low and high Hg contents along the riverbed. As described in Figure 5 and pointed out by Pattelli et al. (2014) for the 2012 flood, Hg pulses and floods are almost systematically in phase. The variability of metal dispersal associated to the effects of flood-sediments sorting and the mixing of particulate-associated pollutants, may result in changes of one to two orders of magnitude in metal content over distances of centimetres (Ciszewski and Grygar 2016). Therefore, overbank deposits and channel bars in the Paglia River represent a secondary source of Hg pollution, leading to the periodical transport of temporarily stored Hg-rich sediments to the river channel and to the floodplain. This phenomenon prevents a decrease of Hg concentration over time at least in short time (i.e., decades). Overbank sediments may indeed represent long-term storage for fine sediments with a residence time of the order of 10^2–10^3 years (Grygar et al. 2016). The constant re-mobilization of contaminated material makes the Paglia River system not very resilient. A similar process is occurring in the Siele Creek, one of the largest Paglia River tributaries (Fornasaro et al. 2022).

Since the contaminated area along the Paglia River almost corresponds with the area identified by the hydraulic hazard map of the Tiber River management basin plan (Trigile et al. 2018; Fig. 6), in the next future it is expected that further Hg mobilization will take place during flood events. The recent broadening of the Paglia River, started in 2010, coincided with an increase in monthly water discharge observed from 2003, consequent of a higher frequency of extreme flood events (Pattelli et al. 2014; Rimondi et al. 2014; Cencetti et al. 2017). These events will be predictably influenced by the variations of the precipitation regime because of climate change (van Vliet et al. 2013; Papalexiou and Montanari 2019). More precisely in southern Europe and in the Mediterranean region it is expected an overall drastic reduction in precipitation, more pronounced in summer (-25-30%; Castellari et al. 2014) Regional-scale model projections for Italy show indeed a significant temperature increases for the period 2070-2100 and a reduction in the number of days with little rain, and, by contrast, an increase of days with heavy rainfall (Castellari et al. 2014). Frequent drought periods characterized by long periods of low water flow, with modest or almost no solid transport, will alternate with intense rainy periods or flash floods, concentrating solid transport in few short events. Consequently, climate variability could contribute to control the Hg distribution and overall mobility from MAMD and the Paglia River floodplain up to the Mediterranean Sea by the way of the Tiber River.

Our study provides useful information for management authorities to define precaution actions (such as limitations of sediment remobilization, river dredging, instream mining) and to identify conservation measures in this area (e.g., tree planting on overbanks, retention basins, thresholds and/or selective weirs). Further monitoring is necessary to ensure that the environmental quality of the river will not be altered by the spatial variability of Hg contaminated sediments distribution. The same strategies can be applied to similar rivers draining metal-contaminated areas that changed their morphology from braided to narrower channel, which in time are likely to act as continuous sources of contaminated particles deposited in their abandoned floodplains. On the other hand, the knowledge of distribution patterns of contaminated sediments is useful to address geomorphologic issues, as they can represent a tracer within the sediment system, providing a useful marker to the extent of sedimentation in a certain period. Furthermore, by tracking the movements, re-working, and removal of these contaminated sediments the role of floodplains as sediment storages can be established at different timescales.

5. Conclusions

The geomorphological and morphodynamic changes of the Paglia River, combined with anthropogenic activities occurred in the last century, controlled the spatial variability of Hg concentration in channel sediments and floodplain deposits of the northern stretch of the Paglia River, downstream the Monte Amiata Mining District. The distribution of Hg observed in the Paglia River floodplain resulted from the interplay of Hg mining, that fed the floodplain with large amounts of Hg-contaminated sediments during the braided stage (end of 1800-mid-1950s) and the subsequent morphological changes of the river, following World War II (including gravel mining and other anthropogenic modifications), that led to the single-channel morphology of the Paglia River. After mine closure, a reduction of Hg concentration over time in river sediments did not occur, as it could be expected. Because of the braided narrowing morphology, the Paglia River enhanced the erosion of old syn-mining terraces, rich in Hg, and redistributed Hg contaminated sediments. Consequently, the process of transport/deposition did not allow a natural “clean up” of the river system since the closure of the mining sites. The temporal and spatial variability of Hg distribution is therefore principally associated with the fluvial geomorphological changes more than to anthropogenic activities.

At present, the main factor controlling Hg distribution in the next future is identified in climate variability, triggering erosion/deposition and redistribution of previously stored Hg contaminated overbank sediments and in the floodplain. In the Paglia River upper section, the alternation of normal flow conditions and flood events affects the geomorphology of the river course contributing to make overbank erosion a permanent secondary source of Hg. The expected intensification of extreme weather events (high rain events, intense floods), consequent of climate change, makes this area a Hg source of remarkable environmental concern at the local (Paglia River), regional (Tiber River), and Mediterranean scales in the future.

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Table

Element	Definition	Reference
Floodplain	The floodplain is formed by past active channel riverbed abandonments. Two mechanisms, lateral migration by the braid-train and reactivation of abandoned channels within floodplains, operating separately or in combination, are responsible for floodplain reworking and their relatively young age (<250 years). Clearly, braided rivers can construct substantial areas of well-developed floodplain.	Aute et al. 2010
River channel	The active channel (or riverbed). The channel through which the water flows.	-
Braided channel	A network of channels formed in a river that has a great amount of sediment and a fluctuating pattern of discharge: the braiding effect is created by the formation of braid bars, around which the individual channels flow.	-
Single channel with low sinuosity	Sinuosity defines the degree of meandering of a riverbed. Channel sinuosity arises from flow hydraulic processes around bends in which secondary, across-channel circulation can increase meander wavelength and the migration of meanders across a floodplain. In general sinuosity is low in confined mountain streams.	Leopold et al. 1964
Overbank sediment	Overbank sediments occur along rivers and streams with variable water discharge. They are deposited on floodplains and levees from water suspension during floods, when the discharge exceeds the amounts that can be contained within the normal channel.	Bolviken et al. 2004
Riverbank	The landform distinguished by the topographic gradient from the bed of a channel along the lateral land-water margin up to the highest stage of flow or up to the topographic edge, where water begins to spread laterally over the floodplain surface.	Florsheim et al. 2008
Bank erosion	Bank erosion refers to the erosion of sediment from riverbank.	Florsheim et al. 2008

Tab. 1 Definition of the geomorphological terms used in the text.

Figures

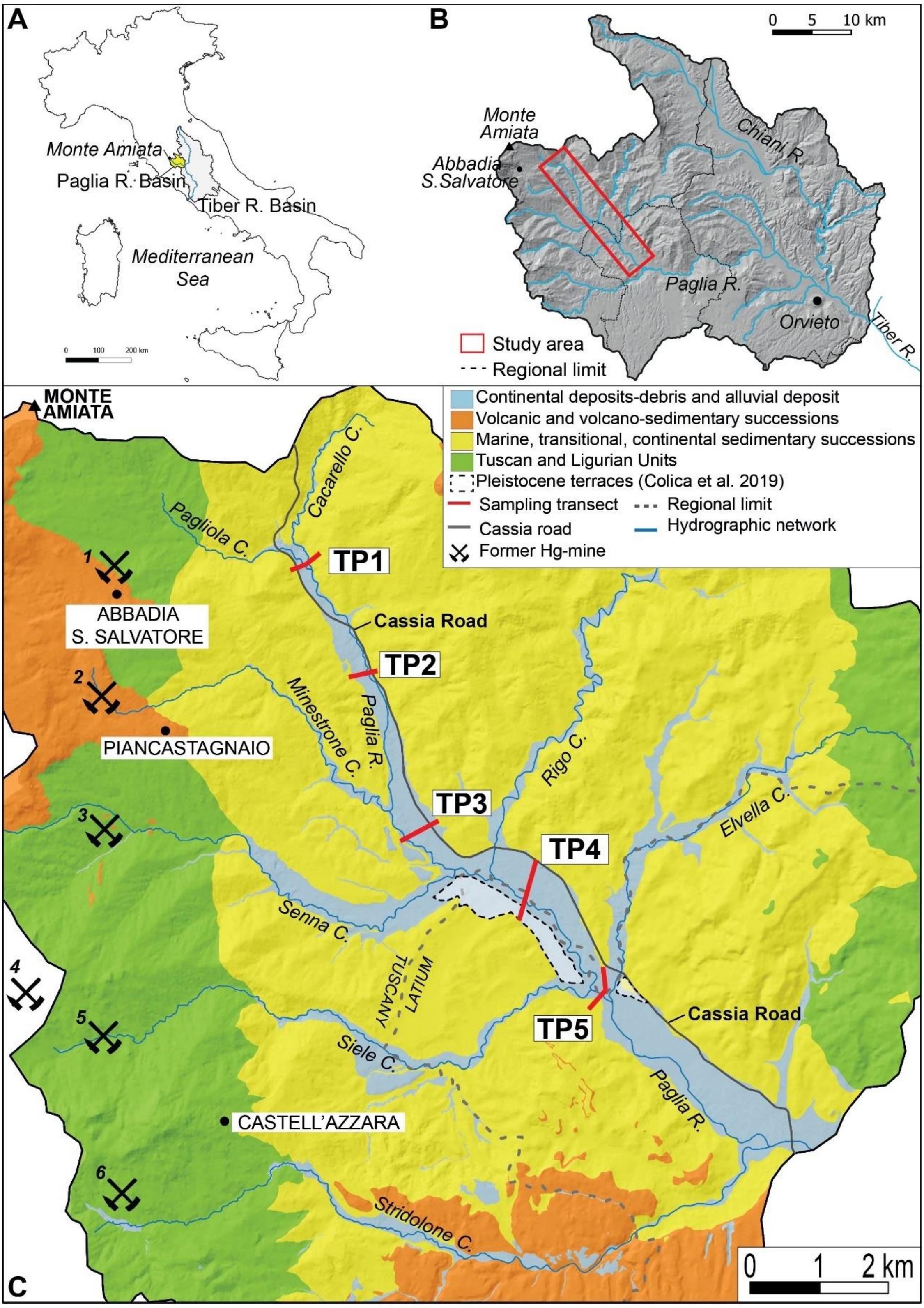


Fig. 1 A) Monte Amiata and Paglia-Tiber system location; B) Paglia River basin and its main tributaries; C) Geological map of the upper part of the Paglia River basin. The location of the sampling transects and of the main mines of MAMD are also reported: 1) Abbadia S. Salvatore; 2) Case di Paolo - Cerro della Tasca; 3) Senna; 4) Solforate; 5) Siele; 6) Cornacchino.

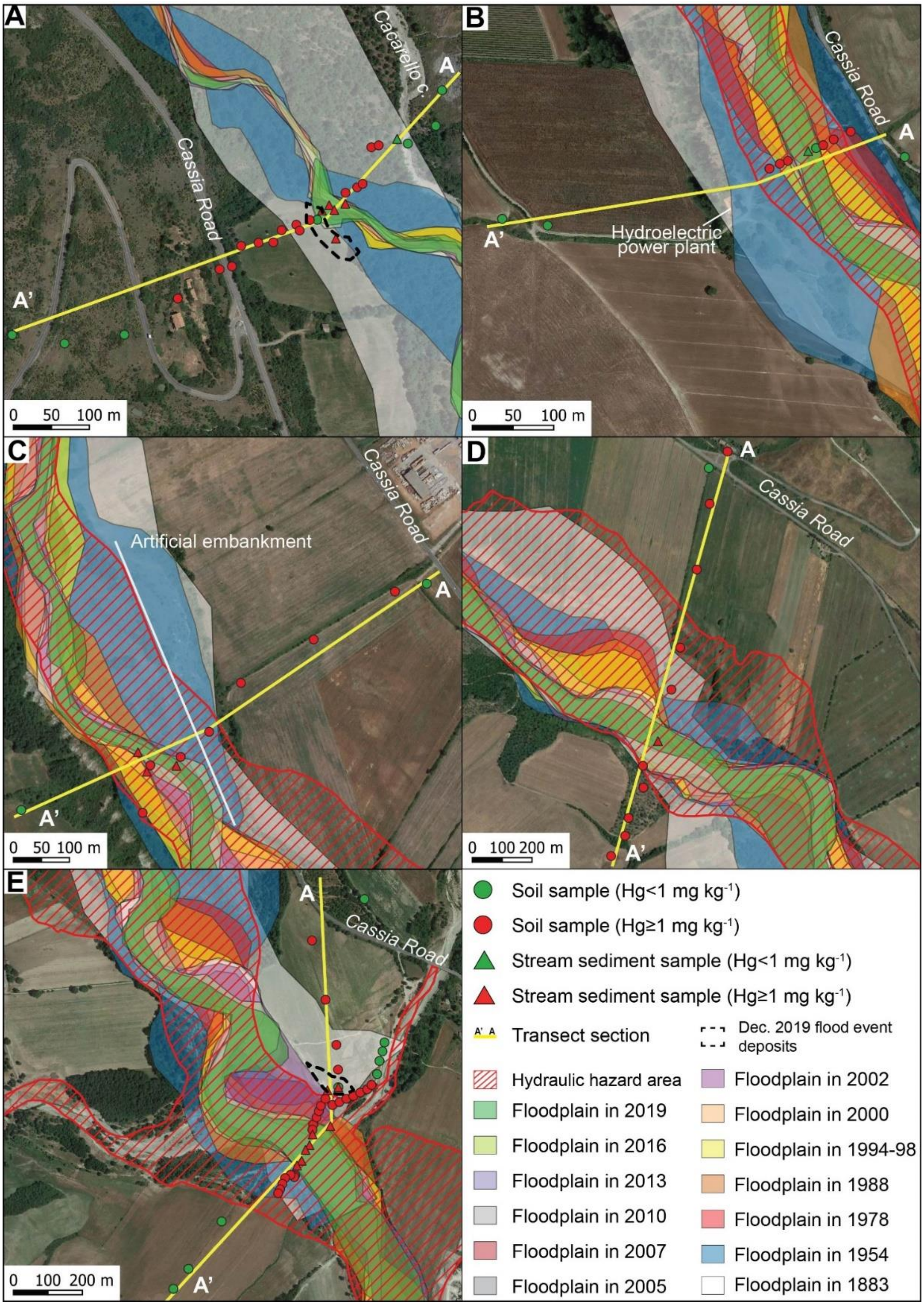


Fig. 2 Satellite image (from Google Maps®, 2019) showing the samples collected along the transects in the Paglia R. A) transect TP1; B) transect TP2; C) transect TP3; D) transect TP4; E) transect TP5. Samples with Hg concentrations lower and higher than 1 mg/kg^{-1} (D.Lgs. 152/2006) are shown in green and red, respectively. The boundary of the riverbed (colored area) in different years from 1954 to 2019, the hydrologic hazard area (lined area), the transects (yellow lines), and the December 2019 flood event deposits (blue dotted line in A and E) are also shown.

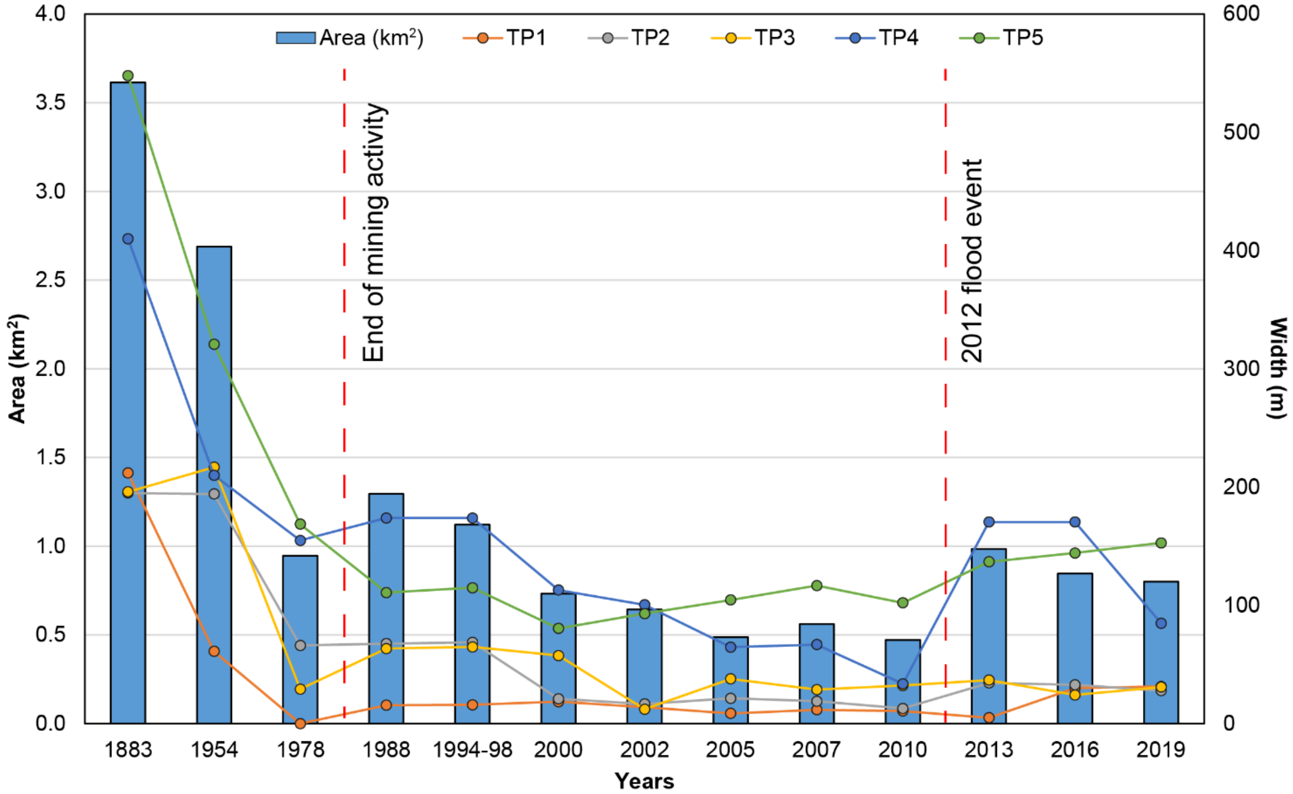


Fig. 3 Floodplain area (m^2) and width (m) along the sampled transects (colored lines) during the 1883-2019 period.

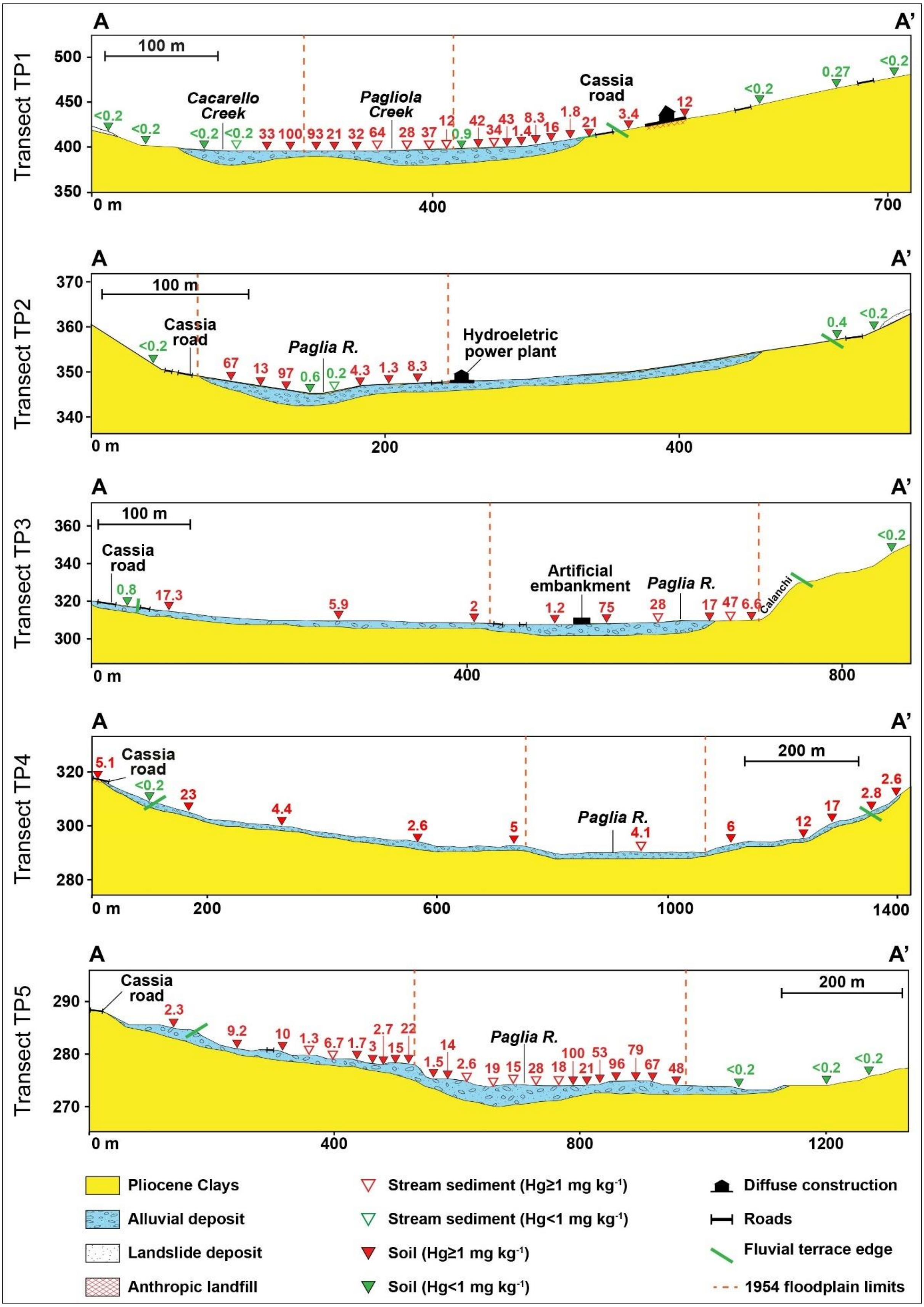


Fig. 4 Geological sections, sample location, and Hg-concentration (mg/kg^{-1}) in soils and sediments sampled along the transects. View from North to South.

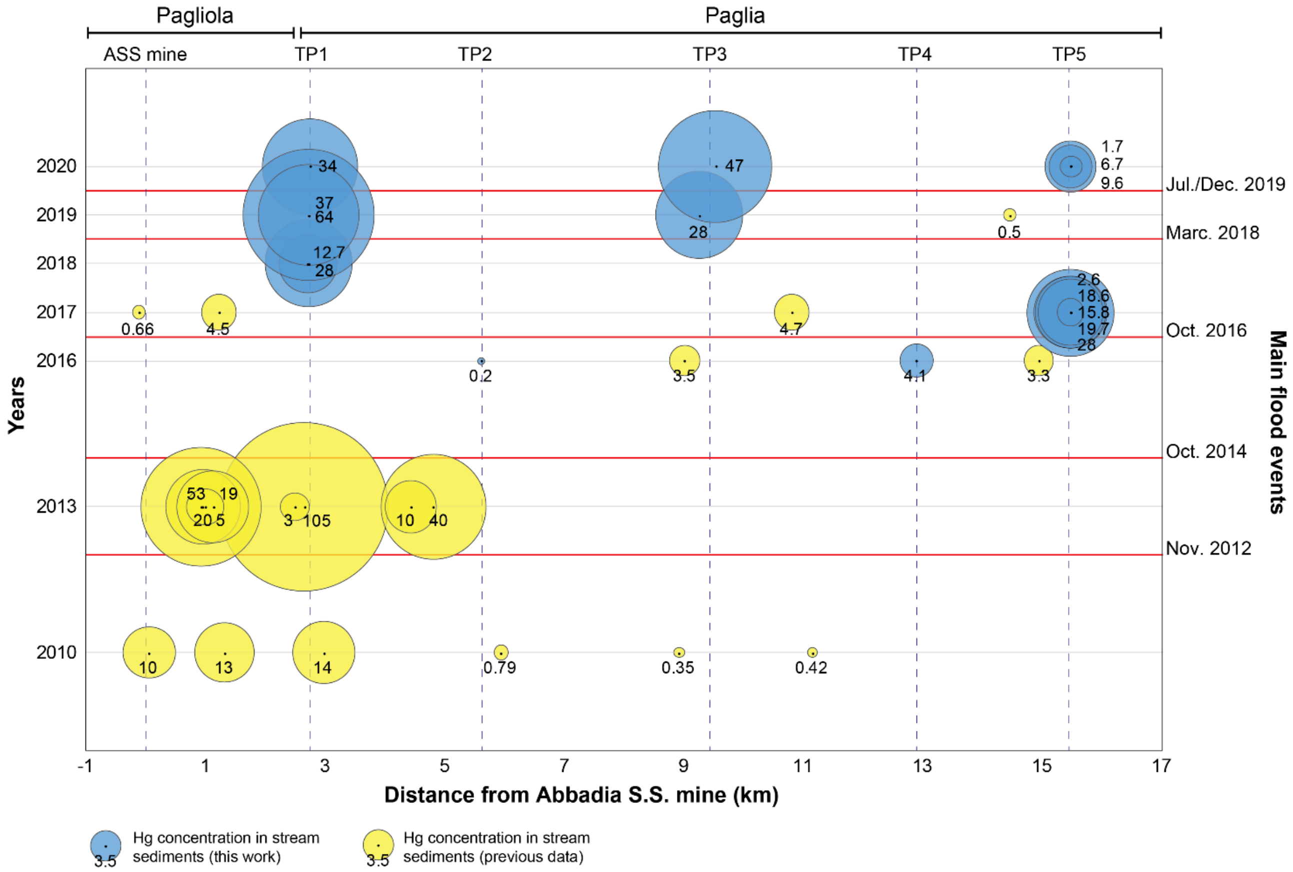


Fig. 5 Time-space variability of Hg concentrations (mg/kg^{-1}) in stream sediments along the Paglia River course in different years. Sampling location is indicated on the top X axis. The main flood events are also reported.

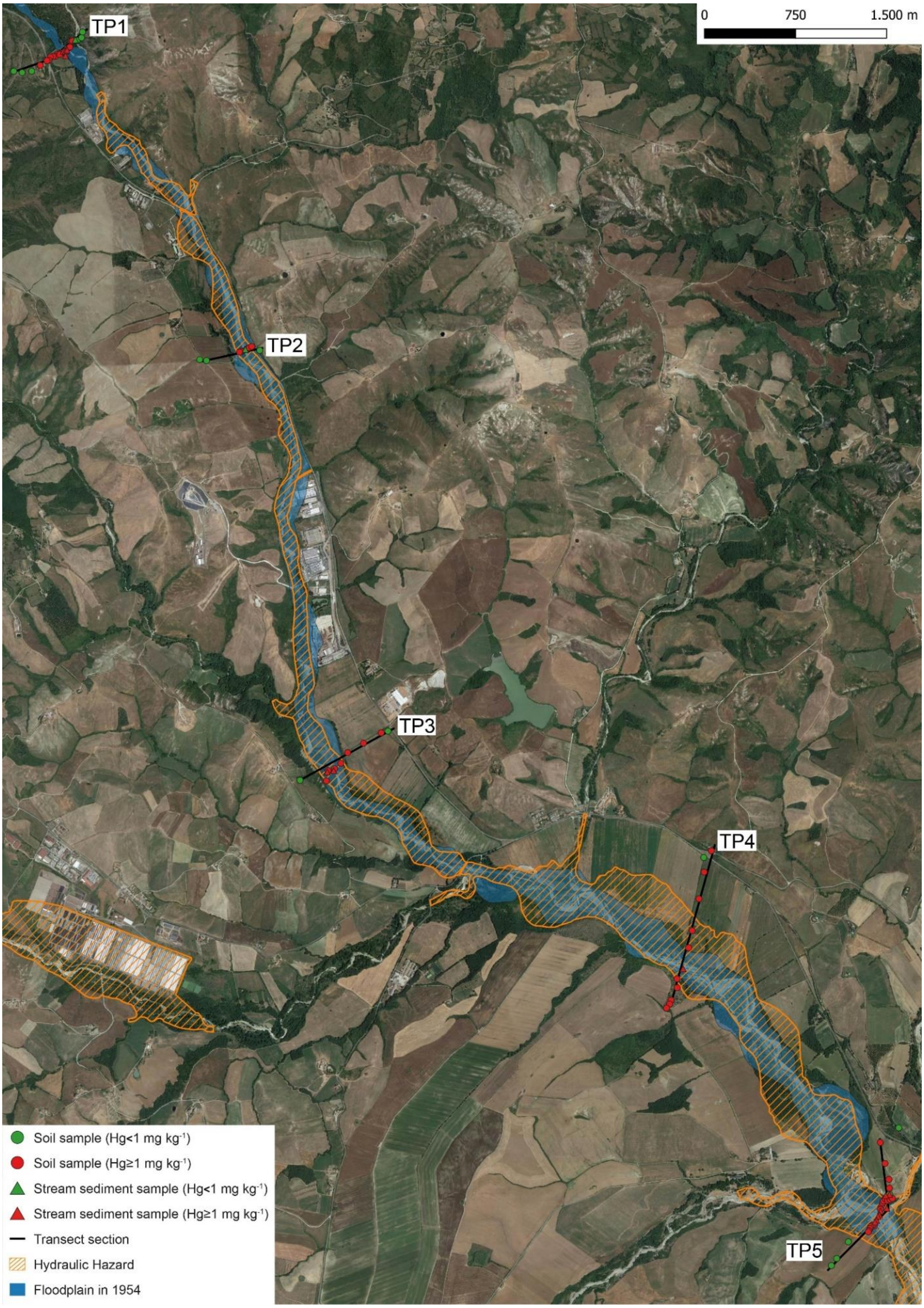
675 
0
750
1.500 m
TP1
TP2
TP3
TP4
TP5
Soil sample (Hg<1 mg kg-1)
Soil sample (Hg≥1 mg kg-1)
Stream sediment sample (Hg<1 mg kg-1)
Stream sediment sample (Hg≥1 mg kg-1)
Transect section
Hydraulic Hazard
Floodplain in 1954

Fig. 6 Hydraulic hazard area (limits of Triglia et al., 2018) and Hg-concentration in stream and soil samples (mg kg^{-1}).

The extensive mercury contamination in soil and legacy sediments of the Paglia River basin (Tuscany, Italy): interplay between Hg-mining waste discharge along rivers, 1960s economic boom, and ongoing climate change

S. Fornasaro[1*], G. Morelli[2], V. Rimondi[1], C. Fagotti[3], R. Friani[3], P. Lattanzi[2], P. Costagliola[1]

1. Dipartimento Scienze della Terra, Università di Firenze, Via G. La Pira, 4, 50121 Firenze, Italy

2. CNR-Istituto di Geoscienze e Georisorse, Via G. La Pira, 4, 50121 Firenze, Italy

3. ARPA Toscana, Area Vasta Sud, Loc. Ruffolo, 53100 Siena, Italy

*Corresponding author: silvia.fornasaro@unifi.it

Abstract

Purpose

The extensive Hg contamination in soil and sediments occurring along the Paglia River (Central Italy) is the result of the interplay between the geomorphological changes of the river and the anthropic activities, primarily associated to the exploitation of Hg-deposits in the Monte Amiata mining district (MAMD). The present study points out the implications of the morphological changes occurred in the last 200 years of the Paglia River on the distribution of Hg along the floodplain and riverbed, which today represent one of the main Hg-reservoirs in the MAMD.

Materials and Methods

The temporal changes of the Paglia riverbed and the extent of its alluvial deposits were reconstructed by a GIS-based analysis of the available maps and aerial photos. The Hg-concentration in soil and sediment samples, collected along five transects transverse to the Paglia River course, was determined by ICP-MS.

Results and Discussion

Samples along the investigated Paglia River segment typically show Hg-contents exceeding the Italian threshold for residential and public green soil use (1 mg/kg^{-1}).

The distribution of Hg in the Paglia floodplain results from the combination of exceedance of sediment yield to the river during mining activities, that fed the floodplain with large amounts of Hg-contaminated sediments during its braided stage about 100 years ago, and the morphological changes of the river, that led to the evolution from a braided to the present-day single channel river.

The magnitude of the extension of Hg-contamination, the river geomorphologic changes, and the processes of transport, deposition, and re-suspension did not allow a natural "clean up" of the river system, which shows a low resilience. Under high flow conditions, and especially in coincidence with intense rain events, large amounts of Hg stored in the overbanks sediments are mobilized and redistributed, contributing to make the floodplain a secondary Hg-source. Extreme weather events, expected to intensify as a consequence of climate change, will contribute to the recurrent distribution of Hg-contaminated legacy sediments in the floodplain and along the Paglia river course.

Conclusion

From a water/land management perspective, the variability of the river flow, associated with an increase of extreme flood events driven by climate change, will affect the distribution of Hg-contaminated particles in the Paglia River, contributing to the Hg input into the Mediterranean Sea in the future.

Keywords

legacy sediments; fluvial dynamics; mercury; Monte Amiata

1. Introduction

Geomorphic features of riverine systems result from the balance of many parameters (e.g., water and total sediment load; Schumm and Harvey 1999; Calle et al. 2017), that may in turn be affected by factors such as climate changes and human activities (Grabowski and Gurnell 2016; Marchamalo et al. 2016; Calle et al. 2017; Owens 2020; Vauclin et al. 2020). Specifically, in fluvial systems draining mining areas, mining activities may contribute significantly to the modification of river morphology, influencing sediment supply and the associated processes of erosion, transport, and deposition (e.g., Ciszewski and Grygar 2016; Davis et al. 2018). In addition, pollutants associated with mining particulate, such as heavy metals, are responsible of large-scale contamination up to several hundred kilometers away from the mining area (Martin and Maybeck 1979; Schafer et al. 2006; Mayes et al. 2013; Rimondi et al. 2019). Mining-contaminated legacy sediments deposited along waterways may remain stored within river channels and on floodplains for hundreds or thousands of years (Salomons and Förstner 1984; Macklin and Lewin 1989; Pavlowsky et al. 2017; Davis et al. 2018; Rimondi et al. 2019). They become diffuse sources of contamination if re-mobilized, for example by overbank erosion during flood events, or by human activities (e.g., gravel mining; Macklin et al. 1997; Pavlowsky et al. 2017; Colica et al. 2019). Floodplains therefore play an important role as both sinks and sources of metal contaminants in mined watersheds (Bradley 1989; Horowitz 1991; Lecce and Pavlowsky 1997; Coulthard and Macklin 2003; Ciszewski and Grygar 2016; Pavlowsky et al. 2017).

In the last 200 years, Italian waterways experienced considerable changes that triggered deep modifications of their original morphology (Surian and Rinaldi 2003; Cencetti et al. 2017, and references therein), similarly to other European rivers (e.g., Garcia-Ruiz et al. 2011; Debolini et al. 2015; Pavanelli et al. 2019). Incision and narrowing of the active channel were the most frequently observed modifications (Cencetti et al. 2017). The Tiber River (central Italy) and its tributary Paglia River ~~(R.)~~ are no exception and were affected by similar processes.

The Paglia River (49 km length) is one of the right-side tributaries of the Tiber River. Its morphological changes play a key role for the delivery of Hg to the Mediterranean Sea, since the river directly collects the runoff from one of the largest Hg ore districts in the world, the Monte Amiata Mining District (MAMD). Previous works described the morphological changes occurred in different sections of the Paglia River (e.g., Cencetti et al. 2017), and the pervasive distribution of Hg in river sediments and soils of the Paglia River floodplain, highlighting how fluvial dynamics contribute to transport Hg contaminated sediments up to 200 km downstream the MAMD (Colica et al. 2019; Rimondi et al. 2019).

The present study points out the implications of the morphological changes in the last 200 years of the Paglia River (Tuscan stretch) on the buildup of the fluvial overbanks, which today represent one of the main Hg reservoirs in the MAMD district. Geochemical data obtained during a sampling campaign conducted in 2020 by the Regional Environmental Protection Agency of the Tuscany (ARPAT) and by the environmental mineralogy group at Dipartimento di Scienze della Terra (DST), Università di Firenze, complement previous

studies by Colica et al. (2019) and Rimondi et al. (2019). These new results were integrated with previous data to assess the spatial and temporal variability of Hg contamination in the Paglia River floodplain.
Specifically, the aims of this study are: i) to understand how the geomorphological (natural and anthropogenic) changes control the Hg distribution in the Paglia River floodplain; ii) to verify the implications of flood events on Hg distribution and resilience of the river system, taking into account the potential consequences of climate changes.

2. Materials and methods

2.1 *Study area*

2.1.1 Tiber-Paglia River system

The Tiber River is the third longest river in Italy, flowing through the city of Rome and into the Mediterranean Sea (Cattuto et al. 1988; Ciccacci et al. 1988; Fredduzzi et al. 2007; Cencetti et al. 2017). The adjustments in its course in the last 250 ky were caused by an interplay between glacio-eustasy, sedimentary processes and regional uplifts (Marra et al. 2019). It was subjected to anthropic pressure probably before the establishment of the Roman Empire (Salomon et al. 2017). The most evident modifications took place during the 20th century and in the last decades following the Italian economic expansion, peaked between 1950 and 1970, with the construction of dams, sediment mining, and changes in the agriculture practices. The morphological changes occurred in the Tiber River are like those observed elsewhere in the Apennine area (Cencetti and Tacconi 2005; Rinaldi and Simon 1998; Surian and Rinaldi 2003).
The Paglia River is one of the right-side tributaries of the Tiber River and arises from the junction of Pagliola an Cacarello creeks (388 m a.s.l., Fig. 1). The former drains the main mining and metallurgical center of MAMD near the Abbadia San Salvatore township. The Paglia River starts its course southeastward along a gentle slope, reaches the border between Tuscan and Latium regions (266 m a.s.l.) about 15 km from the starting point, and it enters into the Tiber River south of the city of Orvieto (Fig. 1C).
The geological-geomorphological structure of the upper basin of the Paglia River is linked to the formation of the Apennines during the Tertiary, and the subsequent post-collisional events (Marroni et al. 2015). The geology of the basin from the base to the top includes (Fig. 1C; Marroni et al. 2015): i) Tuscan and Ligurian Units (Paleozoic – Lower Miocene); ii) marine, transitional, and continental sedimentary successions (Lower Pliocene – Quaternary); iii) volcanic and volcano-sedimentary successions (Upper Pliocene – Upper Pleistocene); iv) continental deposits-debris and alluvial deposit (Quaternary). The quaternary continental deposits are characterized by i) holocenic fluvial deposits, present along the Paglia River valleys and its main tributaries, consisting mainly of sandy-silty beds and pebbles. The Paglia River cuts through its alluvial deposits, locally forming various orders of terraces; ii) Pleistocene deposits: fluvial-lacustrine deposits, mainly formed by conglomerates with sandy-silty beds levels. These deposits are arranged on large terraces located at higher elevation (from 5 to 20 m) compared to the current course of the Paglia River (e.g., Colica et al. 2019). The presence of substrates characterized by erodible lithologies (Mio-Pliocene deposits) contributed to erosion processes with the formation of peculiar morphologies such as the "*biancane*" and the “*calanchi*” (Ciccacci et al. 2009). The shape of the Paglia River basin and the trend of the hydrographic network are

closely correlated with the structural characteristics of the Radicofani and Cetona grabens, set on normal fault systems with NNW-SSE trend, and trend-transforming systems with WSW-ENE trend (Sani et al. 2016). This area is characterized by a Mediterranean temperate climate, with hot and dry summer and cold and rainy winter. The average annual temperature is 10.5°C (period 1953 – 2000), and the average annual precipitation is 1480 mm (over the period 1925 – 2000; Ciccacci et al. 2009). About ⅔ of the total annual precipitation is concentrated in the autumn-winter season (Ciccacci et al. 1988). The Paglia River flow regime is controlled by seasonal variability, ranging from 0.3 $m^3 s^{-1}$ to 26 $m^3 s^{-1}$ monthly average (Fredduzzi 2005), with an annual average discharge of 2.45 m^3/s^{-1} (Cencetti et al. 2017). The hydrological periods are difficult to define (Moretti et al. 1988), due to the torrential regime of the initial part of the Paglia River, that may rapidly reach very high flow, collecting water contributes of a high number of tributaries. In general, the lowest and the highest water flow levels were recorded at the end of the summer period (September-October) and in winter-spring (November-March; Rimondi et al. 2014), respectively. An increase in mean monthly discharge was observed since 2003, due to a higher frequency of extreme flood events (Pattelli et al. 2014; Rimondi et al. 2014; Cencetti et al. 2017). This trend peaked with the flood of 2012 (mean monthly discharge: 91.7 m^3/s^{-1}, peak flow: 2663 m^3/s; Cencetti et al. 2017).
The Paglia River is physically shaped by sequential seasonal events of flooding and drying over a yearly cycle (Gasith and Resh 1999), reflecting the highly irregular rainfall patterns, with marked differences between wet and dry seasons, as most Mediterranean rivers. The concomitance of intense rainy days after dry summer periods, coupled with the scarce vegetation in the area, causes flash floods, with associated sliding-like mud and debris flows (Di Tria et al. 1999).

2.1.2 The Monte Amiata mining district (MAMD)

The MAMD district covers an area of ~400 km^2 and includes 42 former mines and 4 Hg roasting plants (Ferrara et al. 1998). The MAMD produced about 102,000 t of Hg between 1860s and 1980s (Colica et al. 2019), representing the third cumulative production ever reached in the world (Rimondi et al. 2015). The on-site metallurgical processing of cinnabar, the principal ore mineral, produced wastes, called calcines, with significant residual Hg contents (25 – 1500 mg/kg^{-1}; Rimondi et al. 2012; 2015). These wastes were often abandoned or discharged directly into the rivers adjacent to the mines, or used as filling material for road networks, house foundations, or landfills in crops (unpublished report, item T-1268 of the archives of the exploration company RIMIN). Numerous studies highlighted the environmental impact caused by over a century of mining and metallurgical activities in the MAMD, and the consequent contamination of Hg in the sediments transported by the Paglia River (Rimondi et al. 2019, and references therein). The first studies concerning the dispersion of Hg in the rivers of the MAMD date back to Dall'Aglio (1966) and Dall'Aglio et al. (1966), who detected extensive Hg contamination in stream sediments and waters. Bombace et al. (1973) estimated that at least 165 t of Hg were dispersed in the Paglia River from 1954 to 1963, the main period of mining activity. The same authors found up to 10.5 mg/kg^{-1} of Hg in stream sediments in the Paglia River, and up to 71.1 mg/kg^{-1} in the Siele creek, a right-side tributary (Fig. 1C). As stressed by Colica et al. (2019), the Paglia River overbanks sediments represent a secondary pollution source, containing not less than 63 t of Hg.

2.2 Geomorphological and multi-temporal analysis of channel changes

The temporal changes of the Paglia riverbed and the extent of its alluvial deposits were reconstructed by GIS-based analysis of the available maps and aerial photos from the period of maximum mining production to date. Specifically, we used:

- 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.
- Aerial photos taken in 1954 (IGM, scale 1:33,000), coinciding with the maximum production period of MAMD (Caselli et al. 2007).
- Aerial photos taken in 1978 (IGM, scale 1:33,000), coinciding with the final production period of MAMD.
- Aerial photos from 1988 to 2016 (post-production period, during which partial reclamation of two main mining and smelting centers (Siele and Abbadia S.S.) was undertaken).
- Satellite images from Google Earth in 2019 (current status).

Through the open-source software Qgis 3.16 (Hannover; https://qgis.org/it/site/), the main morphological characters of the riverbed and floodplain were vectorized. The result consists of two vector layers: a linear type, representing the riverbed (dashed lines in the figures); and a polygonal one, corresponding to the floodplain (colored fill in the figures). Areas and widths were calculated by using the QGIS *Calculator Field* tool.

In Table 1 we report the definition of all the geomorphological terms used in the text.

2.3. Soil and stream sediment sampling

The geochemical analyses of soil (n = 74) and stream sediments (n = 17) presented in this study combine data of soil and stream sediment collected along five transects transverse to the Paglia River course (TP1, TP2, TP3, T4, TP5; Fig. 1C). New samples were collected from transects studied in previous works by Colica et al. (2019) (TP2 and TP4) and Rimondi et al. (2019) (TP1 and TP5), in the Tuscan portion of the Paglia River basin (Tab. 2).

A new transect (TP3) was chosen to integrate the previous ones. Stream sediments refer to the active Paglia River main course and were collected in the top layer (top 5-10 cm), below the water surface. Soils were collected about every 2 or 3 meters along the transect in the superficial horizon (0-30 cm) of the floodplain. All samples were collected as composite samples of about 1 kg, made up by mixing five sub-samples taken within a square of 5 m side around the selected sampling point, by using a shovel.

2.4 Geochemical analysis

The ARPAT laboratory (Siena, Italy) carried out sample preparation and chemical analysis of collected sediments and soils. Soils and sediments were homogenized, dried in air, sieved with a 2 mm sieve (as required by Italian national guidelines; D.Lgs. 152/2006), and then pulverized with a rotating ball mortar. Following the same Italian national guidelines, Hg concentrations were determined in the fraction <2mm, and were then recalculated to the whole samples (i.e., including the fraction >2 mm). This procedure is mandatory for Italian environmental agencies; in any case, the fraction >2mm was minimal in all collected samples, therefore the application of this methodology had a negligible effect on the analytical results. Prior to analysis, soil and sediment powders were digested in aqua regia in a microwave oven (U.S. EPA 2007; 2014 methods). ~~"Water soluble Hg species" in sediment and soil samples were quantified with leaching tests. These were conducted in deionized water using a soil/sediment to water ratio of 1:10, for a batch reaction time of 24 h, following the methods UNI EN (UNI EN 2004). Since the results denote low water soluble Hg species, these data were not presented in the following.~~

Concentrations of Hg were determined by ICP-MS (Inductively Coupled Plasma Mass Spectroscopy; UNI EN 2016). The ARPAT laboratory is subjected to periodical quality checks by an independent organization (Accredia) according to the standard ISO/IEC 17025 and it takes part to the SNPA interlaboratory network for cross-checking. Specifically for Hg analyses, accuracy is determined employing the certified material ERM CC141 (certified Hg content: 0.083 ± 0.017 mg kg-1; average of laboratory analyses: 0.079± 0.009 mg kg-1). The overall analytical precision of the method is <10%, as determined by replicate analyses of different aliquots of the same bulk sample.

3. Results

3.1 Geomorphological changes along the first section of the Paglia floodplain

Aerial photos and maps from 1883 to 2019 allowed to reconstruct the temporal changes of the riverbed and the floodplain along all the transects, as shown in Figure 2, whereas changes in land-use and geomorphologic features around each transect are reported in the supplementary material (Fig. S1-S5). In the following, we will analyze the temporal changes of the Paglia River floodplain, with reference to area variations. Changes in the floodplain width measured along transects were also considered; however, local features and/or fluctuations (e.g., due to climate variability) may affect the general processes controlling this parameter.

In the investigated segment of the Paglia River, the main changes observed during the 1883–2019 time frame include anthropogenic intervention and modifications in the principal road network, building of an industrial area that occupies part of the river valley, modifications of crop field extension, and other changes in land use (see supplementary materials for further details).

Figure 3 shows that a reduction of the floodplain area occurred from the end of 1800. The decrease was more pronounced between 1954 and 1978, with a reduction of almost two thirds (about 62%) of the total area (from 2.8 to 0.9 km^2). After 1978, which broadly corresponds to the end of mining activity, the floodplain area was subjected to fluctuations, with a relative increase in the period 1988-1998 followed by a progressive slow decrease lasting about 15 years and concluded in 2010. After this year until today, the area increased. Specifically, in the three years from 2010 to 2013, the floodplain area doubled its extension (Fig. 3).

On the other hand, in the period 1883-2010 the riverbed experienced a distinct narrowing of its width at all the five transects (Fig. 3; Fig. S1-S5), with a marked reduction occurred between 1954 and 1978. In the following period, the riverbed width remained more or less constant in the upper part of the river, from transect TP1 to TP3. On the contrary, in correspondence with transect TP5, we notice a progressive enlargement (47%) since 2000, while after the confluence with the Senna Creek, at transect TP4, the width of the Paglia River increases, especially during or after major flood events (e.g., after the 2012 flood).

3.2 Mercury concentrations in stream sediments and floodplain soils

Stream sediments and soils sampled along the transects in the Paglia River show highly variable Hg contents (from <0.2 mg/kg to 100 mg~~/~~kg^{-1}). In Figure 4 the spatial distribution of Hg in sediments and soils along each transect is represented in association with their elevation and lithology. The full dataset is reported in Table S1.

The highest concentration of Hg in stream sediments (64 mg~~/~~kg^{-1}) was recorded at TP1, while in soils (100 mg~~/~~kg^{-1}) at transect TP5. Elevated Hg concentrations (1.7-6.7 mg~~/~~kg^{-1}) were also found in fine sediments collected along transect TP5. These sediments were deposited by a flood event in December 2019, which occurred shortly before the sampling campaign (January-February 2020). This event led to the partial flooding of the field on the left side of the Paglia River.

In correspondence of the transects the Paglia River floodplain is almost entirely anomalous in Hg, i.e. with concentrations above the legal limit (1 mg~~/~~kg^{-1}) defined by the Italian law for soil for residential and green area use (D.Lgs. 152/06), as shown in Figures 2 and 4. The anomaly boundary can be identified with the pre-anthropic fluvial terraces dated to the Pleistocene (Colica et al. 2019). These Pleistocene terraces are located at higher topographic levels with respect to more recent terraces formed during periods of anthropic activity (Colica et al. 2019). Nevertheless, Hg anomalies (> 1 mg~~/~~kg^{-1}) are exceptionally found at high topographic altitude and, in some instances, over the Pleistocene terraces (e.g., in the transects TP4 and TP5), typically nearby roads and houses (Fig. 4).

4. Discussion

4.1 Geomorphological river changes: anthropogenic and natural control and impact on Hg distribution in the floodplain

Braided rivers reflect the ongoing adjustment to fluctuating flow and sediment yield, under high sediment delivery conditions coupled with lower sediment throughput, due to a gentle slope (Piegay et al. 2006). Before the mid-1950s, the Paglia River was characterized by several anastomosing channels, river bars and islands, extending over a large area, as observed in the 1883 maps (Fig. S6; cf. Cencetti et al. 2017). This braided stage of the Paglia River coincided with the period during which Hg production, and thus waste production, at MAMD reached its maximum. Conceivably, sediments delivered by MAMD mining and metallurgical activities played an important role in shaping the changes of the Paglia River floodplain. Local miners report that, throughout the mine activity, mining and metallurgical wastes were discharged along the local waterways during rainy periods, and eventually were collected by the Paglia River. Consequently, peaks of Hg production significantly impacted sediment yields in the Paglia River. One of the main production peaks occurred during the first decades of 1900, driven by the increasing demand of Hg fulminate employed during the ~~I~~ World War I. As reported by Caselli et al. (2007), during this period the MAMD overcame Almadén in Hg flask trading. After the economic crisis in 1930, production decreased, and maintained low during the ~~II~~ World War II, since the district was heavily bombed. After the war, the Hg market, and thus MAMD, had a new important pulse due to the Korean war (Caselli et al. 2007), up to the mid-1960s; in the 1970s the Hg demand began a constant decrease down to a complete halt, with the consequent closure of the mines and plant production site in 1982.

The actual mass of the mine wastes produced can be roughly estimated from the total amount of Hg produced (102,000 tons), by the average Hg content of the *tout-venant* (generally less than 1 wt. %; Strappa 1977), and by the metallurgical recovery rate (about 80%; Benvenuti and Costagliola 2016). Based on this scenario, about $12*10^6$ tons of mining/metallurgical wastes may have been produced in the MAMD, corresponding to $6*10^6$ m^3 of sediments (average density: 2 t~~/~~m^{-3}), the same order of magnitude of the sediment volume presently stored in the fluvial terraces of this waterway (cf. Colica et al. 2019). These estimates suggest that during its braided stage, in the northern stretch of the Paglia River the sediment input was probably high, and significantly contributing to consolidate the braided stage of the river for the first half of 1900s.

In the 1954-1978 timespan, the Paglia floodplain area dramatically shrunk, dropping from 2.6 km^2 to less than 1 km^2 (Fig. 3). The following change to a single channel led to a significant reduction of the floodplain area and produced a local incision of its original valley, leaving most Hg contaminated sediments in its terraces, located at a higher level with respect to the present-day watercourse.

The decrease of the Paglia River floodplain extension was one of the most intense ever recorded compared to floodplain reduction occurred in other Italian rivers (see "phase II" described by Surian et al. 2009). The Paglia River underwent an average reduction of the channel width of about 64% from 1883 to 1954, followed by a further reduction of about 70% from 1954 to 2012. As a result of floodplain narrowing, the Paglia River changed from a pre-1950 braided morphology to the present day wandering single-channel river with low sinuosity (Fig. 2; Fig. S1-S6).

Our study is consistent with the scenario depicted by Cencetti et al. (2017) in the southern stretch of the Paglia River from the Tuscan/Latium border to Orvieto (Fig. 1B), where incision of the Paglia riverbed was enhanced by the erosion of the old floodplain consequent to the increase of gravel mining into the riverbed and recovery of land for agriculture, which reduced supplies of sediment and caused a deficit in sediment transport (Cencetti et al. 2017; Colica et al. 2019). The tendency to riverbed incision is actually a common phenomenon observed in the same period in many other Italian and Mediterranean rivers (e.g., Brenta, Piave, Cellina, Tagliamento, and Torre Rivers in Italy; and Rambla de la Viuda in Spain), mainly steered by gravel mining (Surian and Rinaldi 2003; Aringoli et al. 2015; Cencetti et al. 2017; Calle et al. 2017; Dang et al. 2014). Gravel mining was intense in Italy starting from 1950s up to 1980s (Surian et al. 2009), driven by the post ~~II~~ World War II economic expansion, and impacted river hydromorphologies, leading to scarcity of sediments, unbalanced river systems and modification of the long-term river morphodynamics, long after cessation of gravel mining of the riverbed (e.g., Calle et al. 2017).

The change from a braided to a single channel river had a profound consequence on the distribution of Hg contamination in the Paglia River basin. ~~Gradual deepening and narrowing of this single fluvial channel left Hg-contaminated sedimentary bodies suspended at higher levels than the channel itself.~~ Due to the gradual deepening and narrowing of this single fluvial channel, Hg-contaminated sediments were deposited at higher topographically levels than the channel itself. One of the main consequences of this process led to a change in the transport/deposition cycle and to a tendential loss of mobility of the material deposited on the overbanks. Therefore, nowadays Paglia River contaminated sediments in the overbanks are no longer reached by the water flowing along the river channel, except during flood events. The extent of the overbank deposits impacted by Hg pollution, broadly corresponds to the floodplain built up by the river during the past century. More precisely, along the examined transects, the extension of Hg contaminated sediments roughly coincides with the 1954 floodplain.

Additionally, anthropogenic intervention may have contributed and still contributes to the unusual Hg contamination (Hg ≥ 1 mg~~/~~kg^{-1}; D.Lgs. 152/2006) in areas not subjected to the direct influence of the Paglia River and its tributaries, i.e., at higher elevations than those reached by the Paglia River during floods, and at a higher elevation than the terraces formed in the last century. This is observed almost systematically where transects intercept streets or houses, such as near transects TP1 and TP5. Construction works such as road embankments or foundations of houses may indeed contain anomalously high values of Hg, because between 1954 and 1978 it was common practice the use of mining and metallurgical waste as building material.

Another contribution to the dispersion of Hg can be ascribed to the indirect effect of agricultural practices (soil amendments, irrigation, or artificial drainage), that may have caused the rearrangement and redistribution of superficial soil layers and associated Hg in fields located in the alluvial floodplain (e.g., Montagne et al. 2009).

In summary, our study indicates that the effectiveness with which Hg-contaminated sediments were entrapped/stored along the Paglia River is probably the result of an incidental interplay between i) Hg mining, that fed the Paglia River floodplain with large amounts of Hg-contaminated sediments during its braided stage, and ii) the economic expansion of Italy after the ~~II~~ World War II and the subsequent changes of the morphological features of Paglia River (due to gravel mining and other anthropogenic modifications), that enhanced the change to a single channel morphology of the Paglia River.

4.2 Implications of flood events on Hg distribution and resilience of the river system

Local river morphology, sediment input and runoff, land uses and climate variability control fluvial dynamics (Schumm and Harvey 1999; Grabowski and Gurnell 2016, Marchamalo et al. 2016; Calle et al. 2017; Owens 2020). After the closure of Hg mining, the spatial pattern of Hg downstream the Paglia River became a function of floods and high-water events rather than of Hg released to the river from mining activity (dashed black areas in Fig. 2). In the last 10 years, flood events occurred along the Paglia River caused the erosion of part of the previously built river terraces (Pattelli et al, 2014; Cencetti et al. 2017; Colica et al. 2019). During the 2012 flood, in the lower section of the Paglia River (after the Siele creek confluence), the riverbed temporarily occupied part of the 1954 floodplain, reactivating several bars (as for example at TP5, Fig. S5). The incremented high erosion capacity caused an enlargement of the local river channel. Additional examples of the substantial changes on the width of the riverbed were observed after a flood event in December 2019, when the collapse of the riverbanks and part of the Cassia Road, about 3 km upstream of the TP2 transect, occurred.

The impact of floods on river morphology in the northern segment, highlighted in Figure 3, led to the increase of the Paglia floodplain area after the 2010 flood. A similar phenomenon was observed by Cencetti et al. (2017) in the southern stretch of the river, emphasizing that floods may partially restore the Paglia riverbed extension. These authors observed that by reactivating sediment supply, floods may restabilize channel morphology to near-reference conditions (i.e., pre-1954, pre-single channel), adjusting fluvial landforms as a response to the new hydrodynamic conditions (Simon 1989; Simon and Rinaldi 2006; Calle et al. 2017). Floods indeed play a crucial role in reshaping the patterns of pollutants dispersal, eroding, and transporting contaminants temporarily stored in channel and on overbanks to the floodplain (Coynel et al. 2007; Novakova et al. 2015; Ciszewski and Grygar 2016; Ponting et al. 2020). In river systems draining mining areas, storm and flood events have a significant control on the episodic transport of contaminants, and the impacts have been described in other Hg mining districts (e.g., Širca et al. 1999; Whyte et al. 2000; Springborn et al. 2011; Singer et al. 2013; McKee et al. 2017). During floods, enormous quantities of Hg-contaminated particulate are mobilized because of higher runoff and the increased capacity of the stream to erode riverbanks. Following erosion, Hg transported as particulate suspended matter may increase up to 80-fold (Whyte et al. 2000).

In the Paglia River, a distinct increase in Hg content was recorded immediately after the 2012 flood in stream sediments collected around transect TP1, with up to 905 mg/kg^{-1} of Hg, with respect to pre-flood values of 14 mg/kg^{-1} (Pattelli et al. 2014). Similarly, after a flood event in 2019, mud deposited in the fields close to transects TP5 and TP1 was characterized by Hg content up to 6.7 mg/kg^{-1} and 34 mg/kg^{-1} respectively (Fig. 2A and E, dotted areas). This recurrent phenomenon is highlighted in Fig. 5, showing that high Hg pulses in stream sediments are recorded during or shortly after floods along the northern stretch of the Paglia River.

Figure 5 shows, in addition, that a marked increase in Hg in stream sediments is observed in connection with the main flood events occurred since 2010. On the other hand, in the last years a decrease of Hg concentration has not occurred with increasing distance from the mine site of Abbadia San Salvatore, as could be expected by a “natural clean up” of the system.

Under normal water flow conditions, Hg associated to the Paglia stream sediments is progressively washed away or diluted by a solid load that is not anomalous in Hg. The shifts between normal flow and flood events enhance the erosion of Hg-rich old (syn-mining) terraces, representing the actual overbanks in some part of the river, causing an alternance of low and high Hg contents along the riverbed. As described in Figure 5 and pointed out by Pattelli et al. (2014) for the 2012 flood, Hg pulses and floods are almost systematically in phase. The variability of metal dispersal associated to the effects of flood-sediments sorting and the mixing of particulate-associated pollutants, may result in changes of one to two orders of magnitude in metal content over distances of centimetres (Ciszewski and Grygar 2016). Therefore, overbank deposits and channel bars in the Paglia River represent a secondary source of Hg pollution, leading to the periodical transport of temporarily stored Hg-rich sediments to the river channel and to the floodplain. This phenomenon prevents a decrease of Hg concentration over time at least in short time (i.e., decades). Overbank sediments may indeed represent long-term storage for fine sediments with a residence time of the order of 10^2–10^3 years (Grygar et al. 2016). The constant re-mobilization of contaminated material makes the Paglia River system not very resilient. A similar process is occurring in the Siele Creek, one of the largest Paglia River tributaries (Fornasaro et al. 2022).

Since the contaminated area along the Paglia River almost corresponds with the area identified by the hydraulic hazard map of the Tiber River management basin plan (Trigile et al. 2018; Fig. 6), in the next future it is expected that further Hg mobilization will take place during flood events. The recent broadening of the Paglia River, started in 2010, coincided with an increase in monthly water discharge observed from 2003, consequent of a higher frequency of extreme flood events (Pattelli et al. 2014; Rimondi et al. 2014; Cencetti et al. 2017). These events will be predictably influenced by the variations of the precipitation regime because of climate change (van Vliet et al. 2013; Papalexiou and Montanari 2019). More precisely in southern Europe and in the Mediterranean region it is expected an overall drastic reduction in precipitation, more pronounced in summer (-25-30%; Castellari et al. 2014) Regional-scale model projections for Italy show indeed a significant temperature increases for the period 2070-2100 and a reduction in the number of days with little rain, and, by contrast, an increase of days with heavy rainfall (Castellari et al. 2014). Frequent drought periods characterized by long periods of low water flow, with modest or almost no solid transport, will alternate with intense rainy periods or flash floods, concentrating solid transport in few short events. ~~The contraction of the periods of snow will also affect river dynamics (Billi and Fazzini 2017).~~ Consequently, climate variability could contribute to control the Hg distribution and overall mobility from MAMD and the Paglia River floodplain up to the Mediterranean Sea by the way of the Tiber River.

Our study provides useful information for management authorities to define precaution actions (such as limitations of sediment remobilization, river dredging, instream mining) and to identify conservation measures in this area (e.g., tree planting on overbanks, retention basins, thresholds and/or selective weirs). Further monitoring is necessary to ensure that the environmental quality of the river will not be altered by the spatial variability of Hg contaminated sediments distribution. The same strategies can be applied to similar rivers draining metal-contaminated areas that changed their morphology from braided to narrower channel, which in time are likely to act as continuous sources of contaminated particles deposited in their abandoned floodplains. On the other hand, the knowledge of distribution patterns of contaminated sediments is useful to address geomorphologic issues, as they can represent a tracer within the sediment system, providing a useful marker to the extent of sedimentation in a certain period. Furthermore, by tracking the movements, re-working, and removal of these contaminated sediments the role of floodplains as sediment storages can be established at different timescales.

5. Conclusions

The geomorphological and morphodynamic changes of the Paglia River, combined with anthropogenic activities occurred in the last century, controlled the spatial variability of Hg concentration in channel sediments and floodplain deposits of the northern stretch of the Paglia River, downstream the Monte Amiata Mining District. The distribution of Hg observed in the Paglia River floodplain resulted from the interplay of Hg mining, that fed the floodplain with large amounts of Hg-contaminated sediments during the braided stage (end of 1800-mid-1950s) and the subsequent morphological changes of the river, following World War II (including gravel mining and other anthropogenic modifications), that led to the single-channel morphology of the Paglia River. After mine closure, a reduction of Hg concentration over time in river sediments did not occur, as it could be expected. Because of the braided narrowing morphology, the Paglia River enhanced the erosion of old syn-mining terraces, rich in Hg, and redistributed Hg contaminated sediments. Consequently, the process of transport/deposition did not allow a natural “clean up” of the river system since the closure of the mining sites. The temporal and spatial variability of Hg distribution is therefore principally associated with the fluvial geomorphological changes more than to anthropogenic activities.

At present, the main factor controlling Hg distribution in the next future is identified in climate variability, triggering erosion/deposition and redistribution of previously stored Hg contaminated ~~sediments in the overbanks~~ overbank sediments and in the floodplain. In the Paglia River upper section, the alternation of normal flow conditions and flood events affects the geomorphology of the river course contributing to make overbank erosion a permanent secondary source of Hg. The expected intensification of extreme weather events (high rain events, intense floods), consequent of climate change, makes this area a Hg source of remarkable environmental concern at the local (Paglia River), regional (Tiber River), and Mediterranean scales in the future.

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660 **Table**

Element	Definition	Reference
Floodplain	The floodplain is formed by past active channel riverbed abandonments. Two mechanisms, lateral migration by the braid-train and reactivation of abandoned channels within floodplains, operating separately or in combination, are responsible for floodplain reworking and their relatively young age (<250 years). Clearly, braided rivers can construct substantial areas of well-developed floodplain.	Aute et al. 2010
River channel	The active channel (or riverbed). The channel through which the water flows.	-
Braided channel	A network of channels formed in a river that has a great amount of sediment and a fluctuating pattern of discharge: the braiding effect is created by the formation of braid bars, around which the individual channels flow.	-
Single channel with low sinuosity	Sinuosity defines the degree of meandering of a riverbed. Channel sinuosity arises from flow hydraulic processes around bends in which secondary, across-channel circulation can increase meander wavelength and the migration of meanders across a floodplain. In general sinuosity is low in confined mountain streams.	Leopold et al. 1964
Overbank sediment	Overbank sediments occur along rivers and streams with variable water discharge. They are deposited on floodplains and levees from water suspension during floods, when the discharge exceeds the amounts that can be contained within the normal channel.	Bolviken et al. 2004
Riverbank	The landform distinguished by the topographic gradient from the bed of a channel along the lateral land-water margin up to the highest stage of flow or up to the topographic edge, where water begins to spread laterally over the floodplain surface.	Florsheim et al. 2008
Bank erosion	Bank erosion refers to the erosion of sediment from riverbank.	Florsheim et al. 2008

661 Tab. 1 Definition of the geomorphological terms used in the text.

662

Figures

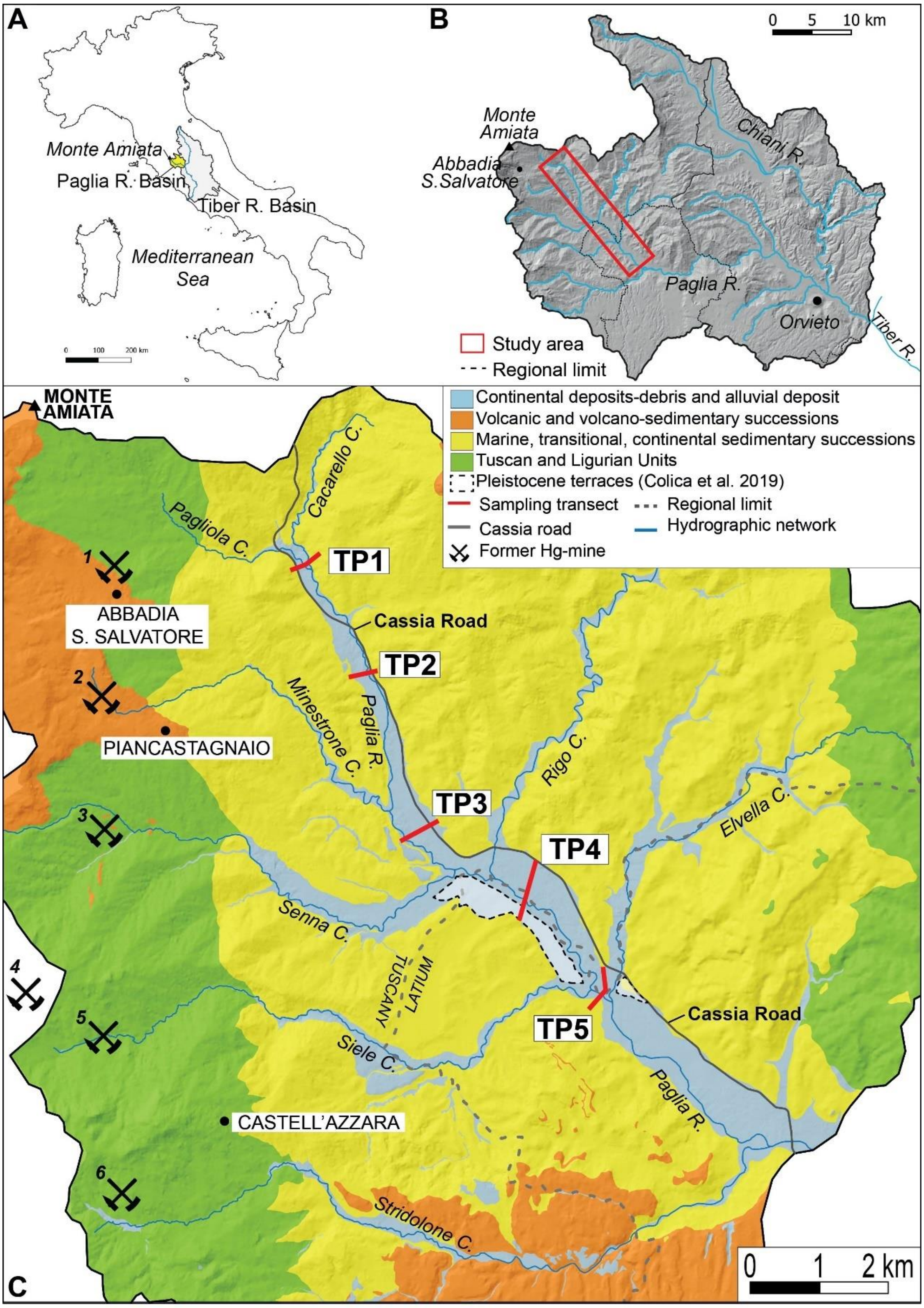

Fig. 1 A) Monte Amiata and Paglia-Tiber system location; B) Paglia River basin and its main tributaries; C) Geological map of the upper part of the Paglia River basin. The location of the sampling transects and of the main mines of MAMD are also reported: 1) Abbadia S. Salvatore; 2) Case di Paolo - Cerro della Tasca; 3) Senna; 4) Solforate; 5) Siele; 6) Cornacchino.

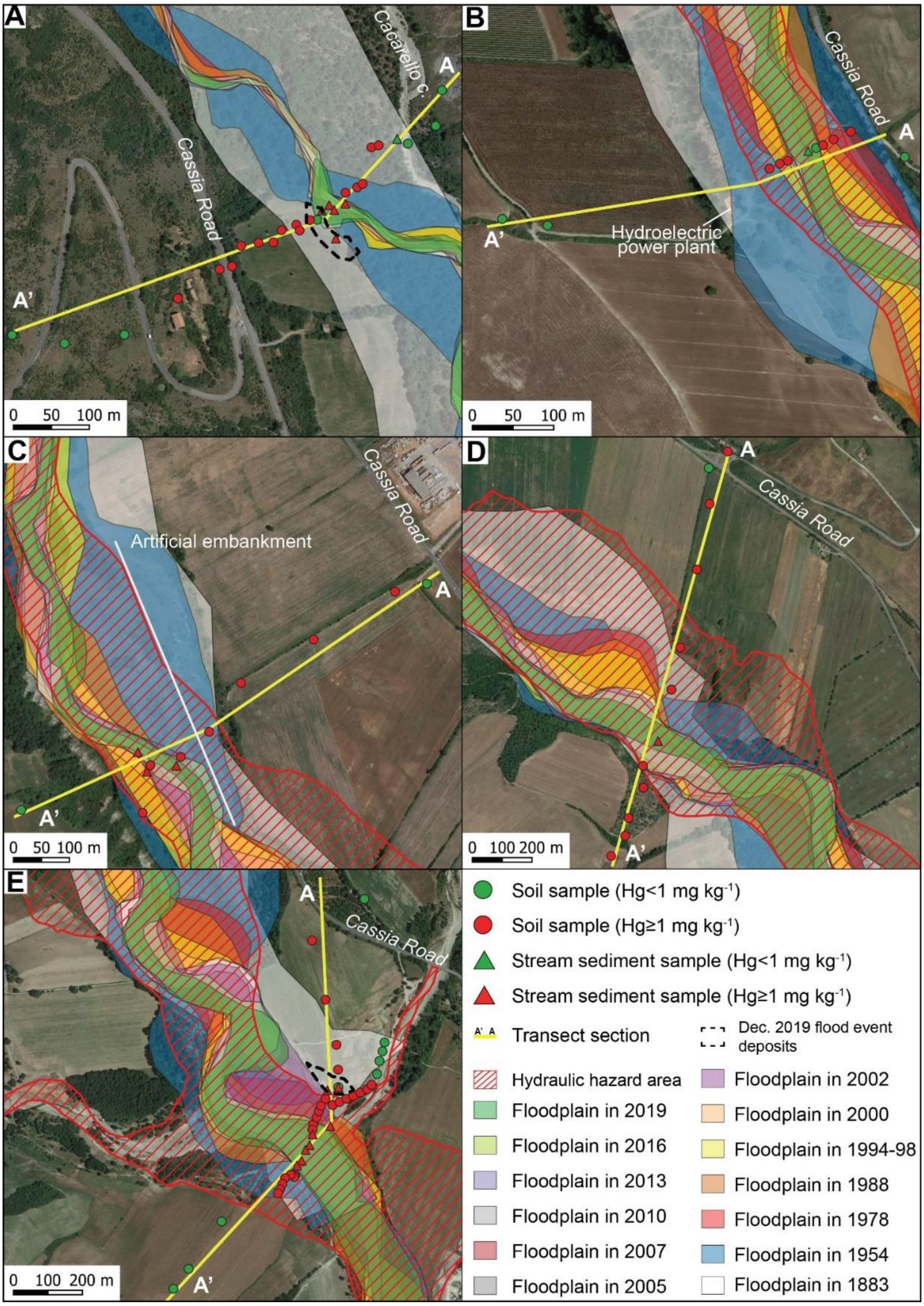

Fig. 2 Satellite image (from Google Maps®, 2019) showing the samples collected along the transects in the Paglia R. A) transect TP1; B) transect TP2; C) transect TP3; D) transect TP4; E) transect TP5. Samples with Hg concentrations lower and higher than 1 mg/kg^{-1} (D.Lgs. 152/2006) are shown in green and red, respectively. The boundary of the riverbed (colored area) in different years from 1954 to 2019, the hydrologic hazard area (lined area), the transects (yellow lines), and the December 2019 flood event deposits (blue dotted line in A and E) are also shown.

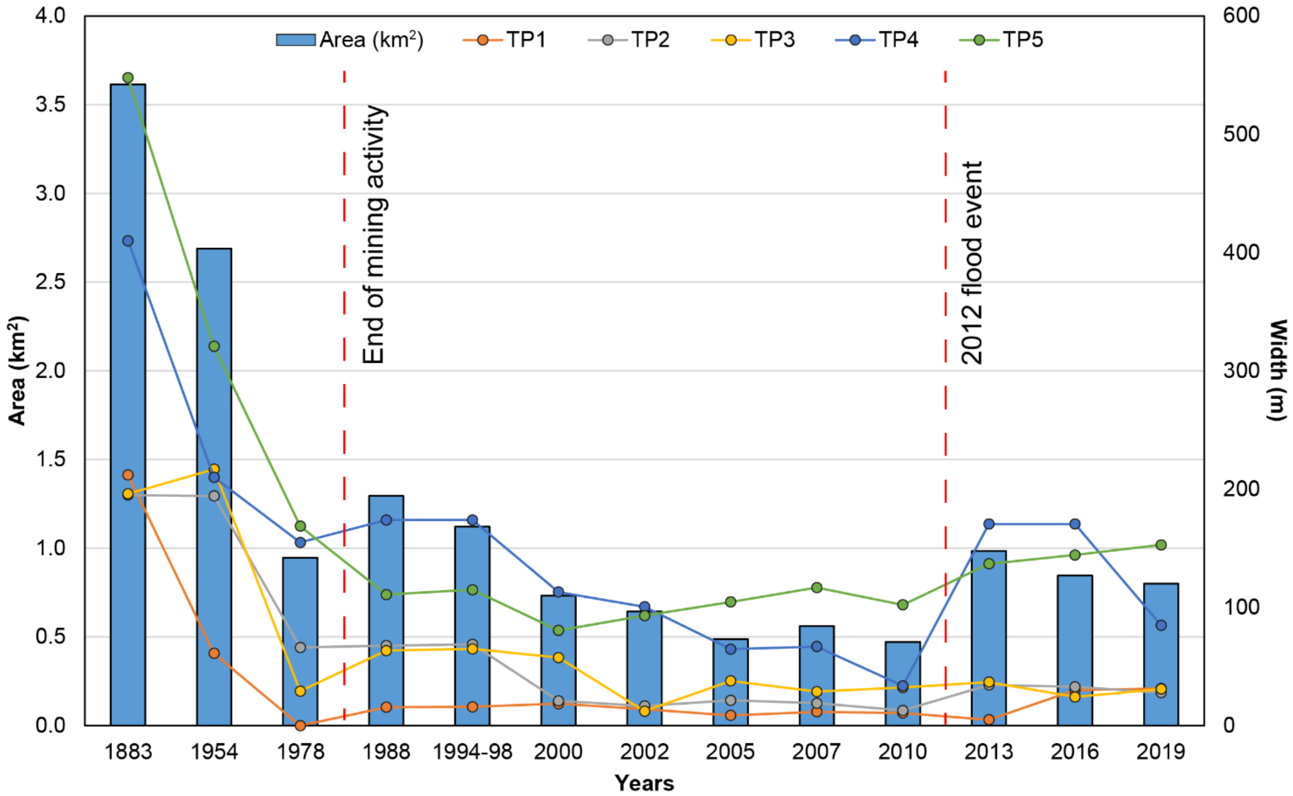

Fig. 3 Floodplain area (m²) and width (m) along the sampled transects (colored lines) during the 1883-2019 period.

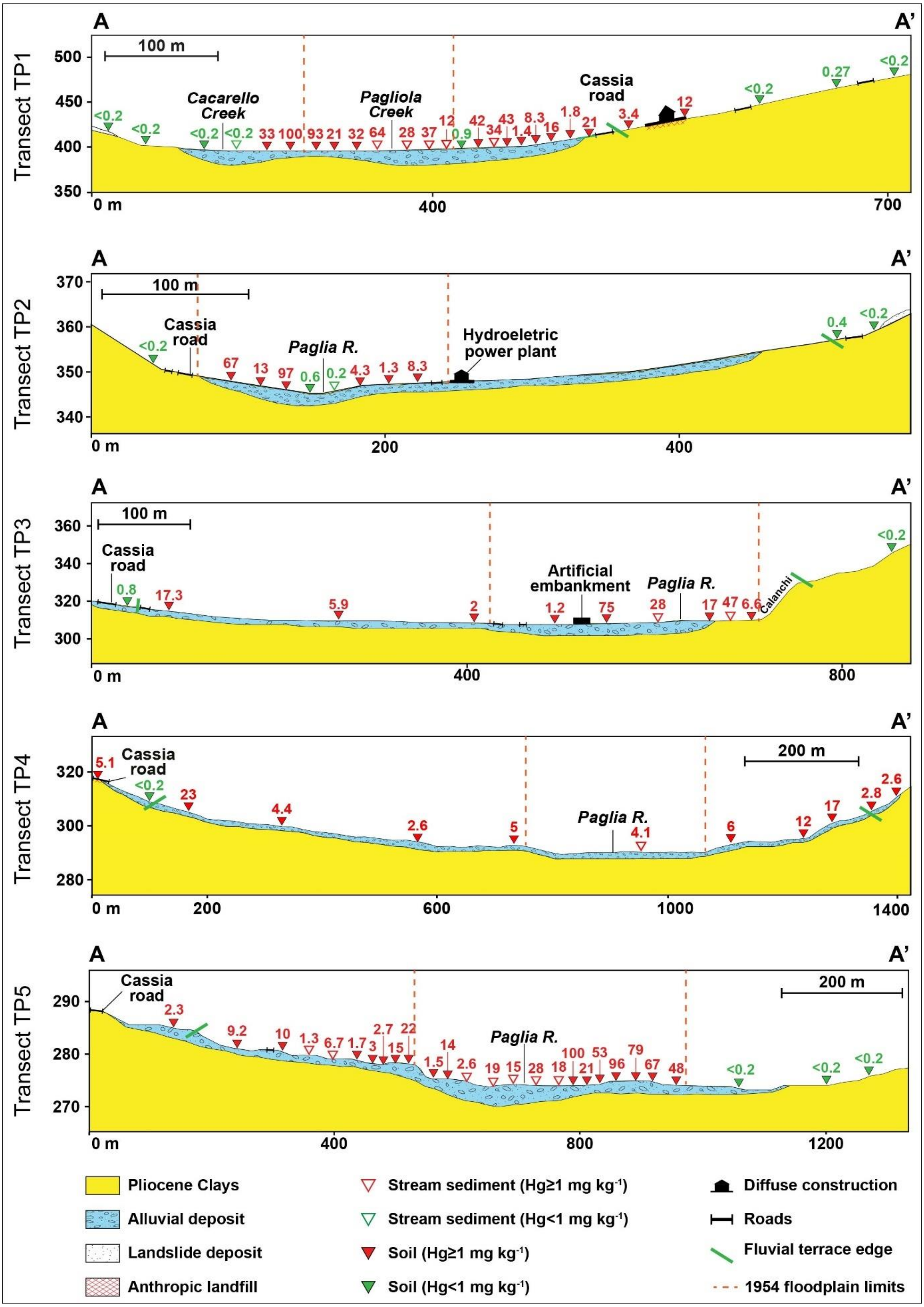

Fig. 4 Geological sections, sample location, and Hg-concentration (mg/kg^{-1}) in soils and sediments sampled along the transects. View from North to South.

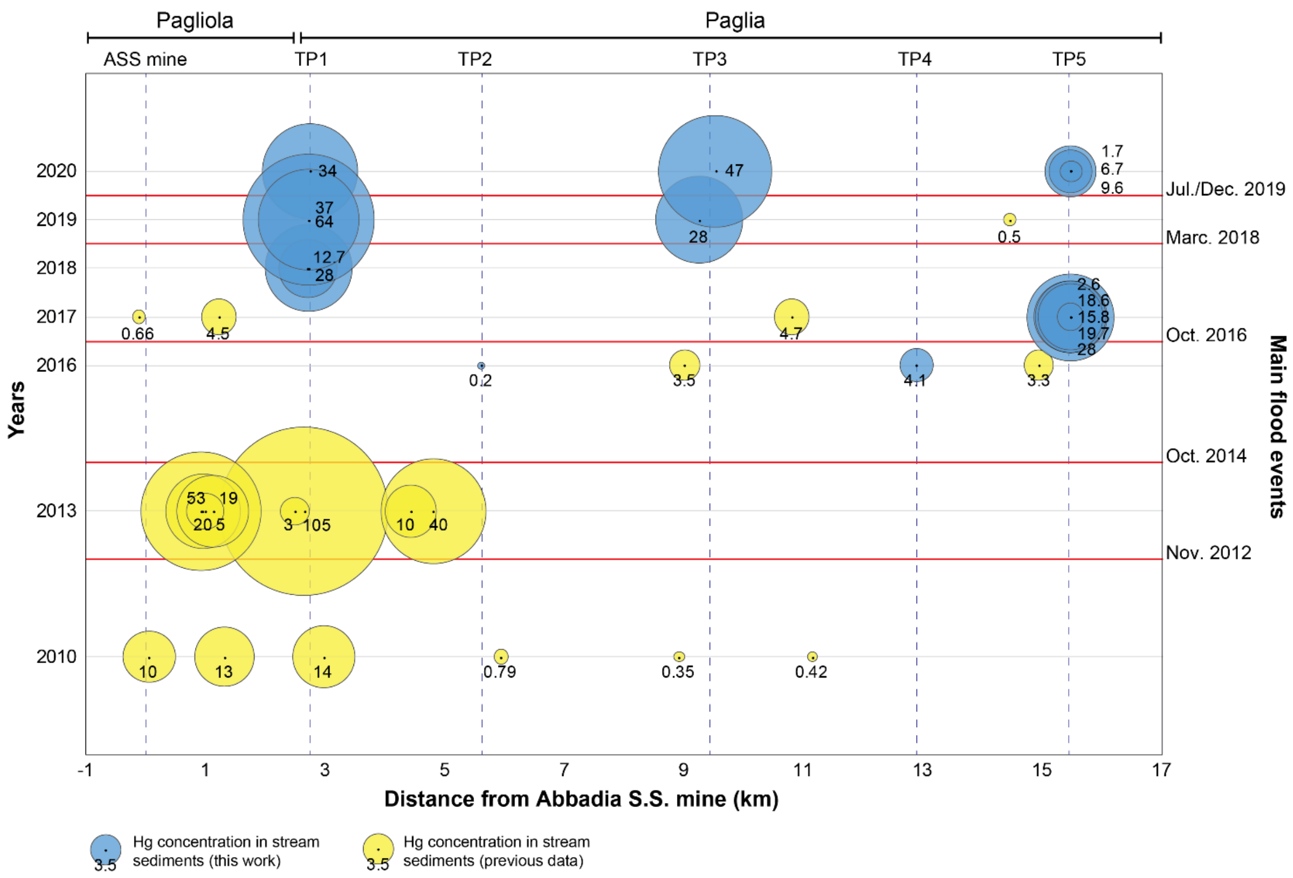

Fig. 5 Time-space variability of Hg concentrations (mg/kg^{-1}) in stream sediments along the Paglia River course in different years. Sampling location is indicated on the top X axis. The main flood events are also reported.

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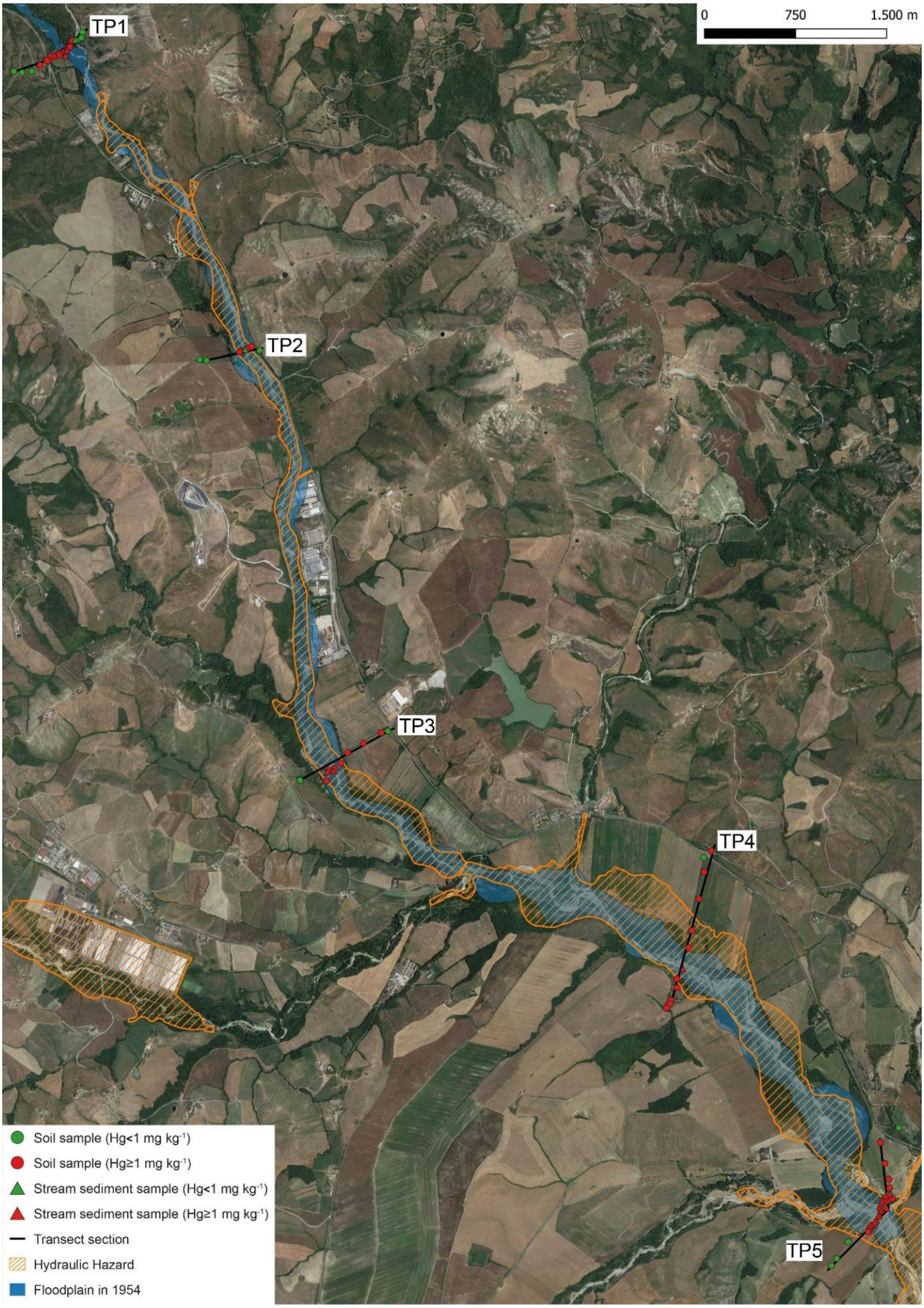

0
750
1.500 m
TP1
TP2
TP3
TP4
TP5
Soil sample (Hg<1 mg kg-1)
Soil sample (Hg≥1 mg kg-1)
Stream sediment sample (Hg<1 mg kg-1)
Stream sediment sample (Hg≥1 mg kg-1)
Transect section
Hydraulic Hazard
Floodplain in 1954

Fig. 6 Hydraulic hazard area (limits of Triglia et al., 2018) and Hg-concentration in stream and soil samples (mg/kg^{-1}).