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Riparian trees in mercury contaminated riverbanks: An important resource for sustainable remediation management

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ABSTRACT

Mining operations generate sediment erosion rates above those of natural landscapes, causing persistent contamination of floodplains. Riparian vegetation in mine-impacted river catchments plays a key role in the storage/remobilization of metal contaminants. Mercury (Hg) pollution from mining is a global environmental challenge. This study provides an integrative assessment of Hg storage in riparian trees and soils along the Paglia River (Italy) which drains the abandoned Monte Amiata Hg mining district, the 3rd former Hg producer worldwide, to characterize their role as potential secondary Hg source to the atmosphere in case of wildfire or upon anthropic utilization as biomass. In riparian trees and nearby soils Hg ranged between 0.7 and 59.9 μg/kg and 2.2 and 52.8 mg/kg respectively. In trees Hg concentrations were below 100 μg/kg, a recommended Hg limit for the quality of solid biofuels. Commercially, Hg contents in trees have little impact on the value of the locally harvested biomass and pose no risk to human health, although higher values (195–738 μg/kg) were occasionally found. In case of wildfire, up to $1.4*10^{-3}$ kg Hg/ha could be released from trees and 27 kg Hg/ha from soil in the area, resulting in an environmentally significant Hg pollution source. Data constrained the contribution of riparian trees to the biogeochemical cycling of Hg highlighting their role in management and restoration plans of river catchments affected by not-remediable Hg contamination. In polluted river catchments worldwide riparian trees represent potential sustainable resources for the mitigation of dispersion of Hg in the ecosystem, considering i) their Hg storage capacity, ii) their potential to be used for local energy production (e.g. wood-chips) through the cultivation and harvesting of biomasses and, iii) their role in limiting soil erosion from riparian polluted riverbanks, probably representing the best pragmatic choice to minimize the transport of toxic elements to the sea.

1. Introduction

The overall material output of human activities defined as “global anthropogenic mass” outweighed all of Earth’s living biomass in 2020 (Elhacham et al., 2020). Sand, gravel, and crushed rock constitute the largest component of the anthropogenic mass and they are the most extracted solid materials (Torres et al., 2021; Přikryl, 2021). Projects that advance the energy transition affect surface hydrology, sediment transport, and landscape evolution (Shobe, 2022) with mineral extraction and application to construction representing the most significant global geomorphological shaping force of the 21st century and a major contributor to climate change (Müller et al., 2013; Torres et al., 2021). Anthropogenic sediment fluxes from mineral extraction and associated waste, excavations, and dredging in 2015 were 24 times the amount of sediment supplied annually by the world’s rivers to oceans (Cooper et al., 2018; Torres et al., 2021). In the near future, anthropic pressure mainly driven by the increase of worldwide population, the energy transition with the development of renewable energies, the increase of raw materials extraction and climate change mitigation solutions, will introduce new environmental impacts (Oyewo et al., 2020; Owen et al.,

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2023; Schäfer et al., 2022; Shobe, 2022; Torres et al., 2021; Wrobel-Daveau et al., 2022). Ecosystem restoration has consequently become an important tool to overcome the consequence of earth exploitation (Di Maiolo et al., 2020; Jones et al., 2018). However, following large scale disturbances, spontaneous recovery of ecosystems is rarely complete (Jones et al., 2018), highlighting the need of developing appropriate remediation and restoration techniques. Among the consequences of mine areas expansion, the increase in the accumulation of contaminants across fluvial systems will pose challenges to river management for the environmental protection and development of new remediation methods (e.g. Owen et al., 2023; Di Maiolo et al., 2020). Worldwide, many river catchments (about 480,000 km of rivers estimated by Macklin et al., 2023), already impacted by heavy metal contamination from former and ongoing mining and other industrial activities (e.g. Covelli et al., 2001; Donovan et al., 2016; Graf et al., 1991; Gray et al., 2000; Gray et al., 2004; Higueras et al., 2003; Loredo et al., 2010; Mao et al., 2023; Pavoni et al., 2021; Rimondi et al., 2019; Schäfer et al., 2022; Schulte et al., 2024 and references therein), constitute an important laboratory to set up the best strategies in fluvial management. Impacted waterways and related floodplains are indeed quite often un-remediable, because of the huge costs involved in their reclamation, making the best practices to minimize the consequences of pollution one of the most remarkable challenges of geosciences (e.g. Fornasaro et al., 2022d; Di Maiolo et al., 2020; Schäfer et al., 2022; Schulte et al., 2024). River drainage in catchments with abandoned mine sites is a source of heavy metals (e.g., Hg, Pb, Zn) through the transport of particle-bound contaminants up to hundreds km downstream the mine site (e.g. Dauvalter and Rognerud, 2001; Fornasaro et al., 2022a; Gray et al., 2014; Macklin et al., 2023; Rimondi et al., 2019; Schulte et al., 2024), making riverbanks and alluvial plains temporary storage sites for pollutants until they are resuspended during flood events (Colica et al., 2019; Fornasaro et al., 2022d; Lynch et al., 2018; Pattelli et al., 2014; Ponting et al., 2021; Schulte et al., 2024). In those areas, riparian vegetation minimizes the dispersion of contaminants (e.g., Cole et al., 2020; Singh et al., 2021; Török and Parker, 2022), constraining the natural erosion through stabilization of riverbanks, taking up contaminants from riverbank soil and from the atmosphere (e.g. Dosskey et al., 2010; Millán et al., 2014; Obrist et al., 2021; Shotyk et al., 2023) and, limiting the decline of freshwater ecosystems (e.g., Dawson and Lewin, 2023; Hubble et al., 2010; Naiman et al., 2010; Pavlović et al., 2016; Simon and Collison, 2002; Singh et al., 2021; Tolkkinen et al., 2021). In Hg-enriched areas, terrestrial vegetation has a critical function in the biogeochemical cycling of Hg, and it is a significant reservoir for global atmospheric Hg. Vegetation assimilates atmospheric Hg (Hg^0) mostly through stomatal and cuticular uptake by leaves (e.g. Millán et al., 2014; Obrist et al., 2021; Zhou and Obrist, 2021; Zhou et al., 2021). Up to two-thirds of terrestrial Hg emissions are deposited back onto land, predominantly through vegetation uptake (Zhou et al., 2021), with estimates of the global Hg^0 vegetation uptake flux ranging between 1000 and 4000 Mg per year (Feinberg et al., 2022; Obrist, 2007). Mercury mines are among the largest sources of Hg in the environment (Guangle et al., 2006; Gworek et al., 2020; Qianrui et al., 2004; UNEP, 2013). In Hg-contaminated catchments, most arboreal plants show substantial Hg enrichments in their tissues (Fornasaro et al., 2023; Meloni et al., 2023; Rimondi et al., 2020; Zhou et al., 2021), with median Hg concentrations across all vegetal tissues 1.2–5.7 times higher than remote, non-enriched sites (Zhou et al., 2021). Upon plant death Hg transferred to soils and watersheds as organic litterfall (Iverfeldt, 1991; Jiskra et al., 2018; Juillerat et al., 2012; Mikkelsen and Vesho, 2000; Zhou et al., 2021; Zhou and Obrist, 2021; Méndez-López et al., 2023), and it is released in rivers, atmosphere and eventually to ocean sediments (Zhou et al., 2021), with the consequent risk of methylmercury (Me–Hg) bioaccumulation in the food chain (Tada et al., 2023; Ullrich et al., 2001). All these processes may be triggered by climate-related extremes (e.g. several extreme droughts, heat waves, heavy storms) enhanced in recent years in Europe by climate change (EEA - European Environmental Agency, 2024, European Pellet Council). Since floodplains in mine-impacted river catchments, are diffuse sources of contamination (e.g. Grygar et al., 2022; Ponting et al., 2021; Rimondi et al., 2019; Shafer et al., 2022; Schulte et al., 2024), variation of climate conditions will alter the physical, chemical, and biological properties of ecosystems, but also the behavior and distribution of pollutants, potentially increasing their toxicity (Gonzalez-Alcaraz et al., 2015; Noyes et al., 2009; Ponting et al., 2021). Consequently, riparian ecosystems reveal significant vulnerability resulting in the increased frequency of these events (Francisco Lopez et al., 2022). Beside flood-induced remobilization of Hg contaminated particles from riverbanks, a significant return pathway (re-emission) for previously deposited atmospheric Hg (natural or anthropic) is the volatilization and emission of Hg during a wildfire (Howard et al., 2019; Francisco Lopez et al., 2022). Vegetation, litterfall, and soil burning lead to massive emissions of Hg and other pollutants into the atmosphere (Biswas et al., 2007; Kumar et al., 2018), with biomass burning representing about 13% of the total contribution of Hg from natural sources (Francisco Lopez et al., 2022). Riparian vegetation in these areas represents a potential source of Hg, which is however poorly investigated. For example, it has been shown that timber harvesting could increase the ecological risk to Hg exposure (Hg bioaccumulation in the food web) in catchment areas with higher pre-harvest Hg concentrations (Willacker et al., 2019), due to organic matter dispersal. On the other hand, riparian vegetation is an important source of biomass for energy production (e.g., Cartisano et al., 2013; Vaccari et al., 2022). In Italy, most residues managed by the fluvial reclamation consortia during riparian bank maintenance and hydraulic works are disposed along the river course, or in landfills as special wastes, and occasional cuts may occur to produce renewable biomass (Del Giudice and Lindo, 2017; Vaccari et al., 2022).

Although management and remediation strategies for the protection of environmental and water quality in such anomalous areas is a priority for local and national authorities against future challenges posed by climate variability, riparian vegetation functions are not always integrated in plans, which is a significant knowledge gap regarding the efficient implementation of environmental policies such as the European Union Water Framework Directive (Water Framework Directive, 2000, European Commission, 2000) (Tolkkinen et al., 2021). Indeed, the Water Framework Directive of the European Union (WFD, 2000/60/EU) requires protecting and, where necessary, restoring water bodies in order to reach good chemical and ecological status, and to prevent deterioration, but it does not provide regional thresholds for river status (Grygar et al., 2022). In non-remediable Hg contaminated catchments with legacy of historical contamination added knowledge of riparian vegetation ecological services will contribute to the implementation of policy regulations.

In this context, we report here a screening of the Hg contents in riparian trees along the Paglia River (southern Tuscany, Italy), the major river draining the eastern side of the abandoned Mt. Amiata Hg mining district (MAMD), the 3rd former Hg producer worldwide. Sediments and soils in the floodplain and riverbanks are characterized by anomalous Hg concentrations, above the geogenic background of the area (in the order of 1 mg/kg; Montefinese, 2021; Fornasaro et al., 2022c; Fornasaro et al., 2022d). Here, mobilization and redistribution of Hg-contaminated soil and sediments during floods (Fornasaro et al., 2022c, 2022d) make the Paglia River a major contributor of Hg transport from the district to the Tiber River, the largest river in central Italy, and eventually to the Mediterranean Sea through its outlet after Rome (Colica et al., 2019; Fornasaro et al., 2022a; Rimondi et al., 2015, 2019). The riparian vegetation of the study area is mainly represented by poplar forest, willows, alder, oaks, acer, robinia and other species typical of this dynamic habitat (Cartisano et al., 2013). The study focuses mainly on poplars (*Populus* spp.) because they are naturally widespread along the Paglia riverbanks (Cartisano et al., 2013), and they are among the most used species for phytomanagement (e.g., Chalot et al., 2020; Fortier et al., 2016; Robinson et al., 2022) due to their fast growth rates and deep roots. Moreover, they are commonly used for biomass and may end up into wood chips used as a solid biofuel (Del Giudice and Lindo, 2017; Vaccari et al., 2022). In addition, *Robinia pseudoacacia* L. and *Quercus* spp. are investigated, because i) they are also present on riverbanks, ii) are of interest in cutting for wood chips in the area, and iii) they also accumulate heavy metals available in the surrounding environment (e.g. Jonsson et al., 1997; Perone et al., 2018; Środek and Rahmonov, 2021).

The aims of this study are i) to assess the storage of Hg in the trunks of riparian tree plants and topsoils of river banks along the Paglia River, and assess the potential risk as a secondary Hg source to the atmosphere in case of fire; ii) to evaluate how the commercial wood quality of the riparian vegetation is deteriorated by the presence of Hg in soils and river banks for the anthropic utilization as biomasses. As a general outcome by considering the Paglia riverbanks as an exemplifying case study, we highlight the role of riparian vegetation in non-remediable Hg contaminated river catchments as a tool for implementing management practices of contaminated alluvial plains. In view of climate change extreme events, riparian vegetation should have proved to limit riparian soil erosion, decrease contaminants dispersion, maintain water quality along the watershed and represent a trap to limit Hg emissions in the atmosphere, together with being a sustainable resource of biomass for energy production.

2. Materials and methods

2.1. Study area

The Paglia River (southern Tuscany, Italy) is one of the most important tributaries of the Tiber River (Fig. 1), with a catchment area of 1338 km^2. The tract investigated in this study runs from the Paglia River source (made by the confluence between the Cacarello and Pagliola Creeks) to the regional Tuscany-Latium border (Fig. 1). In this stretch (approximately 1.8 km^2) the Paglia River collects most of the runoff from old Hg mine sites of the Mt. Amiata district through the Minestrone, Senna and Siele Creeks. The climate of the area is Mediterranean, with dry summer and wet winter/autumn seasons. Average precipitation (mm) in the last 10 years (2013–2023) recorded at three weather stations in the area was 1048–1547 mm, with its maximum recorded at Mt Amiata station (2092 mm). The river has a torrential regime, with low levels during summer and rapidly increasing high levels after rainfall events. The distribution of the riparian trees along the Paglia riverbanks changes over time because of frequent flooding and/or by human activities, such as hydraulic maintenance works, gravel extraction or clear cuts. The most abundant tree species, identified in a previous work (Cartisano et al., 2013) in a riparian area partly overlapping the area of this study, were: i) uneven-aged poplar forests (*Populus* spp.), localized in the most dynamic areas of the river in association with willows (*Salix* spp.), ii) scattered groups of alder (*Alnus glutinosa* L.) in the most frequently flooded areas without drainage, iii) Turkey oak (*Quercus cerris* L.) coppices, regularly managed for firewood production, located to a greater distance from the river and less disturbed by the river dynamics. Secondary species, like *R. pseudoacacia*, *Acer* spp., *Carpinus* spp, *Fraxinus* spp, *Quercus* spp. and others can also be found (Cartisano et al., 2013).

2.2. Plant material and soil sampling

Five sampling sites, described as 'Casetta', 'pre-industrial area', 'post-industrial area', 'Senna' and 'Centeno', were selected to represent different areas of the Paglia River from its origin to the regional Tuscany-Latium border (Fig. 1). The industrial area is a small industrial district comprising a few small-medium enterprises (kitchen factory, wood chips production). The supplementary file reports detailed information on the specific site features (Table. S1, Fig. S1). Visual observation and species recognition identified poplar (*Populus* spp.), oaks (*Quercus* spp.), and black locust (*R. pseudoacacia* L.) trees as the most abundant species in the selected sites. Other tree and shrub species were present, but they were not considered for sampling because they were scattered and not as abundant. At each site, about 9–13 trees were sampled, for a total of 56 trees (Fig. S1, supplementary material). Samples were collected from at least 4 trees of each species. In the "pre-industrial area", "post-industrial area", and "Centeno" sites (Fig. S1 supplementary material), only two of the selected tree species were present, therefore sampling was limited to these species (poplar and black locust in pre-industrial area and Centeno; poplar and oak in post-industrial area).

Tree cores were sampled using a drill corer (Fig. 2a). Three wood cores (8/10 cm long, 0.5 cm diameter; Fig. 2b) were collected from each individual at about 1–1.4 m height from soil. Cores were put in plastic containers and once in the laboratory were frozen within 8 h from collection until analyzed. One composite (five random samples within one square meter) topsoil sample (in the following indicated as "soils") was collected at each site. Soil replicates were collected at "pre-industrial area" and "Senna" sites.

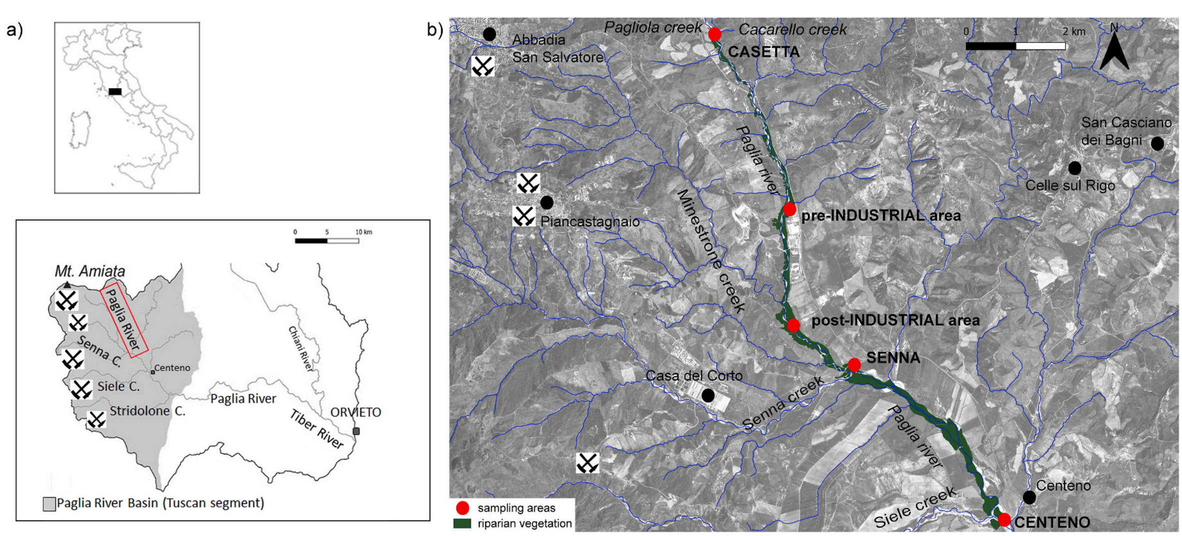

Fig. 1. Map of the study area. a) location of the abandoned mines: 1) Abbadia San Salvatore; 2) Case di Paolo; 3) Senna; 4) Siele; 5) Cornacchino; b) Location of the sampling sites: Casetta, pre-industrial area, post-industrial area, Senna and Centeno. Riparial vegetation (green area) along the Paglia River is estimated using the Territorial and Environmental Information System of Tuscany and Lazio (Territorial and Enviornmental Information System of Tuscany; Regione Lazio, 2015).

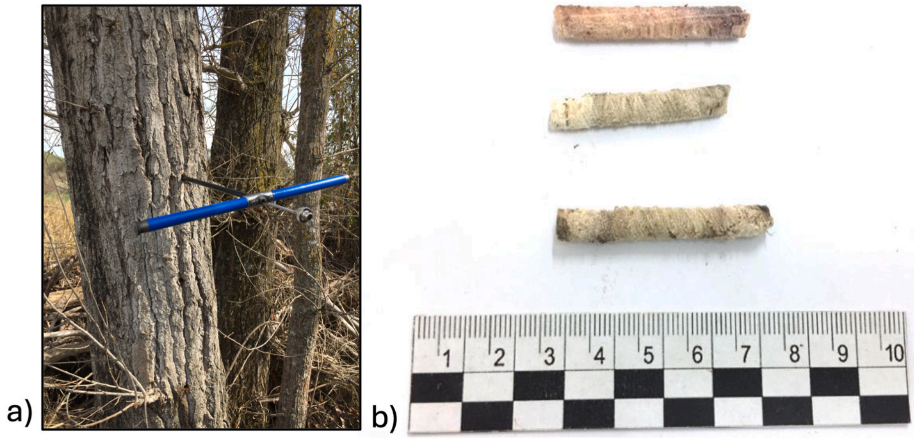

Fig. 2. Photograph of a) sampling drill corer; b) tree cores.

2.3. Analytical methods

Mercury concentrations in tree cores and in soils were determined according to the US EPA 7473 method by thermal desorption with a direct mercury analyser (DMA-80), integrating thermal decomposition, amalgamation, and atomic absorption spectrophotometry. Tree cores were defrosted and left 2 h to dry at air temperature, subsequently the three cores for each tree were finely sliced and homogenized, and 0.1 g of sample was analyzed for Hg. Water content in tree samples was estimated heating about 0.1 g of each sample at 105^{o} C until constant weight and mercury concentrations are reported with reference to dry weight (μg/kg dry weight) (Chiarantini et al., 2016; Rimondi et al., 2020).

Soils were dried at air temperature. Organic matter content in soil was estimated by loss of ignition (LOI), heating at 550 °C for 4 h samples previously dried at 105 °C (Heiri et al., 2001) and organic carbon (OC) was estimated as ½ LOI (%) according to Pribyl (2010). An aliquot of air-dried soil sample (about 0.1 g) was analyzed for Hg with DMA-80.

Precision of trees and soil analyses were ensured by analyzing at least three replicates for each sample. Relative standard deviation (RSD%) was generally within 20%. Results are expressed as the average concentrations of the replicates. Blanks and standard reference materials (NIST SRM 1573a, NIST SRM 1575a for plants and 2711a for soils), were also analyzed to ensure precision and accuracy of the analyses. Analytical precision of replicates of standard materials ($n = 8$ for 1573a; $n = 5$ for 1575a, $n = 2$ for 2711a) was 12%, 4% and 5% RSD%, respectively. Accuracy of standard materials was within 10%. Mean detection limit of the instrument was 0.078 ng Hg.

2.4. Statistical analysis

The variability of Hg concentrations in the collected arboreal species were investigated using the non-parametric Mann–Whitney test, due to the non-normal distribution of data. The test was performed by comparing Hg concentrations recorded in *Populus*, *Quercus*, and *Robinia* trees at each sampling site, to find differences of Hg-uptake by these genera. Furthermore, the statistical correlation was investigated between Hg concentrations in the arboreal species and the Hg content of soils sampled in each site to detect any direct correlations. The correlation was tested with the non-parametric Spearman's correlation coefficient. The analyses were carried out using R-Studio software (R Core Team, 2018), with a significance level equal to 0.05 for all procedures.

3. Results

Measured Hg concentrations (expressed as average of replicate measurements) in trees (μg/kg) and soils (mg/kg) are reported in Table 1 and Table 2. The range of Hg concentrations in trees is 0.7–59.9 μg/kg and the average concentration for all trees is 15.3 μg/kg. Average water content is 37% (Table 1). In *Populus* trees Hg ranges between 2.2 and 59.9 μg/kg, in *Quercus* between 5.1 and 24.7 μg/kg, and in *R. pseudoacacia* between 0.7 and 32.5 μg/kg. Fig. 3 shows Hg concentrations (μg/kg) in all tree species at each site. The highest variability among replicate measurements was found in some samples of poplar trees, with RSD up to 79%. Average Hg concentrations recorded in poplars (22.8 μg/kg*)* and oak trees (13.2 μg/kg) are significantly higher (Mann–Whitney test $p < 0.05$) than those detected in *Robinia* trees (average 7.7 μg/kg) (Fig. 3). Differently, no statistical differences (Mann–Whitney test $p > 0.05$) are observed between Hg concentrations recorded in poplars and oaks.

Average Hg concentrations (μg/kg) of all trees at each site for each species are shown in Fig. 4, together with the suggested limit for high quality wood pellets and chips (100 μg/kg) defined by UNI EN ISO 17225-1:2021, 2021. The boxplots show that concentrations exceeding 100 μg/kg are limited to outliers, and that most values are below 100 μg/kg. Outlier values, ranging between 93 and 738 μg/kg, were found only in poplar trees. Concentrations of Hg in soils range from 2.2 to 52.8 mg/kg, with the highest value at Casetta, and the lowest at Centeno (Table 2). Average Hg concentration in all the sampling sites is 29.7 ± 17.8 mg/kg. We emphasize that the high difference among soil replicates (up to 39% RSD) was already observed for soils in close by areas, due to the "nugget effect" (Rimondi et al., 2019). Organic carbon in soils ranges between 1.5 and 7.7 % (Table 2). Scarce or even absent correlation ($p > 0.05$) is found between Hg concentrations in soils and Hg concentrations in trees; only *Quercus* shows a weak correlation. However, the absence of these trees in some sampling sites strongly affects the results of the statistical elaboration.

4. Discussion

4.1. Mercury sources in riparian trees

Mercury contents in soils found in this study (2.2–52.8 mg/kg) are consistent with previous works, and specifically with the location of sampling sites within the "Hg-impacted corridor" previously defined by Fornasaro et al. (2022c). These values are all above the Italian limit for Hg in residential soil (1 mg/kg, D. Lgs 152/2006-Legislative Decree, 2006). At the selected sites, Hg contribution in soil is mostly associated to the mechanical erosion of sediments from mining areas present in the Paglia River catchment due to runoff, with redistribution during flood events (Colica et al., 2019; Fornasaro et al., 2022d). Indeed, riparian soils along the Paglia River section in Tuscany are impacted by Hg contaminated sediments with up to 185 mg/kg of Hg (Colica et al., 2019; Fornasaro et al., 2022c, 2022d; Rimondi et al., 2019). Soil may contain

Table 1
Mercury concentrations (μg/kg) in the studied trees (average, maximum, minimum, and median values are also reported for all trees and for each species. RSD (%) is the relative standard deviation of the replicates of the same sample.

Location	Sample name	Hg (μg/kg)	RSD (%)	Hg maximum (μg/kg)	Hg minimum (μg/kg)	Water content (%)	Tree Species
CASETTA	CORT2	10.0	7	10.8	9.6	31	*Populus*
CASETTA	CORT3	31.1	67	57.6	13.5	33	*Populus*
CASETTA	CORT4	5.0	3	5.1	4.9	27	*Populus*
CASETTA	CORT5	10.1	10	11.7	8.8	27	*Populus*
CASETTA	CORT1	5.1	14	5.9	4.6	39	*Quercus*
CASETTA	CORT6	19.9	14	23.6	17.0	32	*Quercus*
CASETTA	CAS Q18	21.0	9	23.2	19.8	34	*Quercus*
CASETTA	CAS Q19	24.7	10	26.3	21.8	31	*Quercus*
CASETTA	CAS R20	4.6	10	5.1	4.2	33	*Robinia*
CASETTA	CAS R21	3.4	56	5.6	0.8	28	*Robinia*
CASETTA	CAS R22	9.3	8	10.1	8.6	37	*Robinia*
CASETTA	CAS R23	4.4	5	4.6	4.2	28	*Robinia*
pre-INDUSTRIAL area	PIOP7	22.1	9	24.2	20.4	47	*Populus*
pre-INDUSTRIAL area	PIOP9	47.4	37	78.5	28.8	42	*Populus*
pre-INDUSTRIAL area	PIOP4	23.5	13	28.1	19.4	52	*Robinia*
pre-INDUSTRIAL area	PIOP5	5.0	16	5.9	4.4	21	*Robinia*
pre-INDUSTRIAL area	PIOP6	1.6	62	3.6	0.5	30	*Robinia*
pre-INDUSTRIAL area	PIOP8	1.3	13	1.5	1.2	29	*Robinia*
pre-INDUSTRIAL area	PRE R24	5.2	11	5.6	4.5	31	*Robinia*
pre-INDUSTRIAL area	PRE R25	7.9	13	8.5	6.7	31	*Robinia*
pre-INDUSTRIAL area	PRE R26	7.6	7	8.2	7.2	36	*Robinia*
post-INDUSTRIAL area	PIOP10	33.6	74	76.5	10.5	61	*Populus*
post-INDUSTRIAL area	PIOP11	20.6	59	40.8	7.3	40	*Populus*
post-INDUSTRIAL area	PIOP12	27.8	16	31.9	23.1	54	*Populus*
post-INDUSTRIAL area	PIOP13	20.2	14	22.4	17.1	46	*Populus*
post-INDUSTRIAL area	PIOP14	22.5	44	40.2	11.4	44	*Populus*
post-INDUSTRIAL area	PIOP15	59.9	14	69.2	54.4	38	*Populus*
post-INDUSTRIAL area	POST P1	9.4	13	11.5	7.4	40	*Populus*
post-INDUSTRIAL area	POST P2	12.2	30	18.2	8.1	56	*Populus*
post-INDUSTRIAL area	POST P3	9.4	11	10.4	8.3	33	*Populus*
post-INDUSTRIAL area	POST Q1	10.4	10	11.4	9.4	35	*Quercus*
post-INDUSTRIAL area	POST Q2	11.9	13	13.3	10.3	39	*Quercus*
post-INDUSTRIAL area	POST Q3	5.6	15	6.1	4.6	36	*Quercus*
post-INDUSTRIAL area	POST Q4	7.3	6	7.8	6.9	35	*Quercus*
SENNA	CORT12	19.6	20	23.9	14.6	40	*Populus*
SENNA	CORT13	30.6	1	30.9	30.4	37	*Populus*
SENNA	CORT14	22.3	19	27.1	18.7	32	*Populus*
SENNA	CORT15	11.1	14	12.3	9.4	38	*Populus*
SENNA	CORT16	13.2	13	14.9	11.5	41	*Quercus*
SENNA	CORT17	13.6	51	23.6	7.5	45	*Quercus*
SENNA	SEN Q1	7.5	13	8.7	6.3	39	*Quercus*
SENNA	SEN Q2	5.6	14	6.5	4.8	43	*Quercus*
SENNA	SEN R1	32.5	16	37.5	27.9	19	*Robinia*
SENNA	SEN R2	14.5	1	14.7	14.4	31	*Robinia*
SENNA	SEN R3	6.3	79	16.3	2.7	27	*Robinia*
SENNA	SEN R4	4.3	0.4	4.4	4.3	32	*Robinia*
CENTENO	CORT7	41.1	17	50.0	33.0	58	*Populus*
CENTENO	CORT8	15.9	23	20.0	12.8	35	*Populus*
CENTENO	CORT9	35.5	24	44.7	27.7	49	*Populus*
CENTENO	CORT10	35.6	17	42.0	30.2	48	*Populus*
CENTENO	CEN P31	7.2	9	7.7	6.4	50	*Populus*
CENTENO	CORT11	2.4	60	3.9	0.7	31	*Populus*
CENTENO	CEN R27	5.3	14	6.1	4.6	39	*Robinia*
CENTENO	CEN R28	6.7	19	8.2	5.7	34	*Robinia*
CENTENO	CEN R29	1.6	69	3.7	0.7	37	*Robinia*
CENTENO	CEN R30	0.7	18	0.9	0.6	28	*Robinia*
Average all trees		15.3				37	
Maximum all trees		59.9				61	
Minimum all trees		0.7				19	
Median all trees		10.2				36	
Average Populus spp.		22.8				23	
Maximum Populus spp.		59.9				60	
Average Robinia pseudoacacia		7.7				8	
Maximum Robinia pseudoacacia		32.5				32	
Average Quercus spp.		13.2				13	
Maximum Quercus spp.		24.7				25	

Hg locally derived from the bedrock, and/or mechanically transported by runoff and wind, or else adsorbed from the atmosphere. Moreover, soil receives the litterfall of local vegetation, which, as said above, mostly acquires Hg via the atmospheric path. With respect to the atmospheric contribution, measurements of Hg^0 concentrations in air along the Paglia riverbanks are not abundant (Sinforici, 2021; Rimondi et al., 2019), and are limited to spot surveys. The reported values in the catchment area range from 5 to 62 ng/m^3 (Rimondi et al., 2019), well below those observed at abandoned mine sites, where even recent studies document concentrations exceeding 5000 ng/m^3 (McLagan

Table 2
Mercury concentrations (mg/kg) in soil samples and loss on ignition LOI (%). Organic carbon (OC, %) is calculated according to Prybil et al. (2010).

Location	Sample name	Hg (mg/kg)	RSD (%)	LOI 550 (%)	OC (%)
CASETTA	S-CORT-CAS	52.8	1	15.3	7.7
pre-INDUSTRIAL area	S-CORT-preIND	22.9	19	3.3	1.6
pre-INDUSTRIAL area	S-CORT-preINDb	30.8	38	3.2	1.6
post-INDUSTRIAL area	S-CORT-postIND	24.9	13	2.9	1.5
SENNA	S-CORT-SENNA(Q)	44.3	39	5.7	2.9
CENTENO	S-CORT-CENT	2.2	15	4.8	2.4
Average		29.7		5.9	2.9
Maximum		52.8		15.3	7.7
Minimum		2.2		2.9	1.5

et al., 2019; Cabassi et al., 2022) and up to 16,000 ng/m^3 downstream the Siele mine area (Fornasaro et al., 2022b).

Because of this widespread geogenic Hg anomaly, trees from the Mt. Amiata areas contain more Hg than similar species grown in less affected areas (e.g., Fornasaro et al., 2023; Rimondi et al., 2020). The concentration ranges found are in fact at the upper end of values reported for wood of *Populus* spp. (Table. S2). For instance, Siwik et al. (2010) report average values of 1–4 μg/kg and of 1.6 μg/kg for *Quercus* spp. from four locations in the United Kingdom described as "contaminated". Gustin et al. (2022) report a range of 0.9–1.5 μg/kg for *Populus tremuloides* Michx. at a forest in Sierra Nevada, California. Maillard et al. (2016) report values in the 5–40 μg/kg range for a location impacted by a chlor-alkali plant. Higher concentrations (50–80 μg/kg), like those found in this study, were reported by Petráš et al. (2012) for five riparian locations in Slovakia, and even higher concentrations (up to 280 μg/kg) were reported by Abreu et al. (2008) for an anthropogenically contaminated area in Portugal. The lower Hg concentrations found in

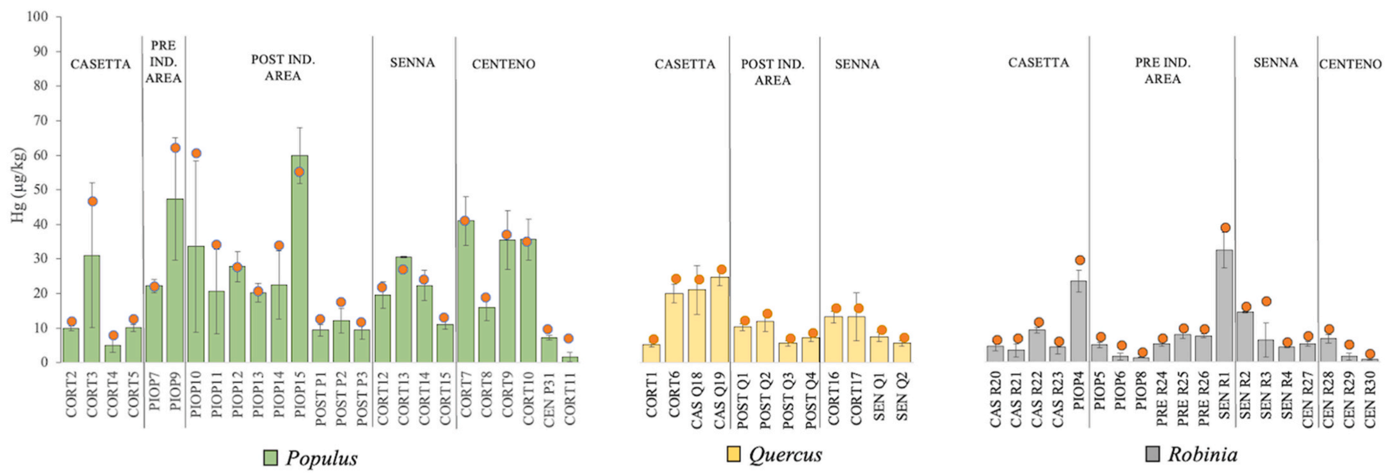

Fig. 3. Mean concentrations of Hg (μg/kg) in each tree. Bars represent the standard deviation (μg/kg) of the mean of replicate measurements of samples. Red dots indicate maximum concentrations (μg/kg) among replicate measurements.

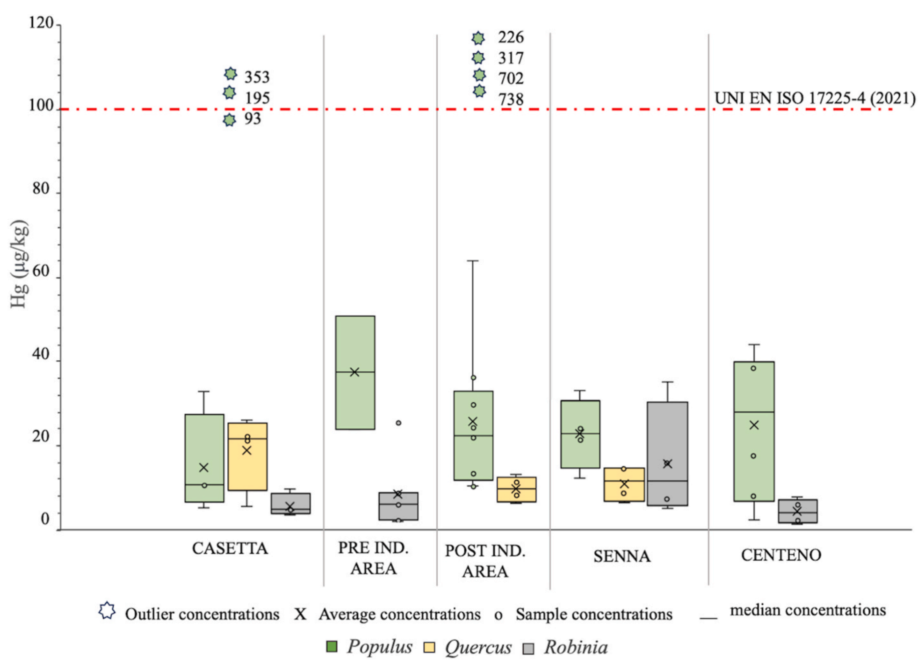

Fig. 4. Boxplots of Hg concentrations (μg/kg) for tree sampled species at each site. Outliers are reported with the related concentration values (μg/kg) at the corresponding site.

R. pseudoacacia trees with respect to the other species are consistent with literature data. This species is a moderate to low accumulator of heavy metals from the soil, it has a deep root system and the ability to fix heavy metals around the roots (e.g. Băbău et al., 2021). The high tolerance of *Robinia* in heavy metals contaminated soils is mainly linked to its roots-rhizobium symbiosis: this microbial community proved to increase heavy metals resistance of this plant, as well as its biomass and N content in tissues (Hao et al., 2015). On the other hand, within the Abbadia San Salvatore former mining area, where the ore was roasted and liquid Hg was produced, maximum Hg concentrations in *Populus* spp. and *R. pseudoacacia* internal trunk samples were 16860 and 680 μg/kg respectively, and average Hg concentrations of soil were 462 mg/kg (Meloni et al., 2023). Mercury uptake by trees occurs through the atmospheric pathway to leaves (as Hg^0 species), and from soil through the root system, the first path being quantitatively prevailing (Assad et al., 2016; Yuan et al., 2022; Zhou and Obrist, 2021; Zhou et al., 2021). The atmospheric contribution may include re-emission from local soil, and transport from more distant sources (e.g. cement production, chlor-alkali plants; Navrátil et al., 2021), including, in this case, the "hotspots" of abandoned mines and geothermal plants (Cabassi et al., 2022; Fornasaro et al., 2023; McLagan et al., 2019). Statistical analysis revealed no correlation between Hg contents in soil and trees, confirming previous results (Siwik et al., 2010; Fornasaro et al., 2023). As reported by Bishop et al. (1998), just over 10% of Hg in soils could be translocated to the aerial parts of trees, while the great part of Hg is taken up and immobilized in the roots (Beauford et al., 1977; Godbold and Hüttermann, 1986; Lindberg et al., 1979; Zhou et al., 2021). Moreover, in the soils around the mining area of Abbadia San Salvatore Hg is mainly found in the form of HgS (Rimondi et al., 2015), a stable and scarcely soluble phase, therefore Hg uptake by roots can be considered negligible. Near Almadén Hg mine (Spain) a dual mechanism of Hg uptake was found, with roots accumulating Hg in proportion to the soil levels, while aerial plant material absorbed Hg vapor directly from the atmosphere (Lindberg et al., 1979). Based on the available evidence we suggest that Hg in the studied trees derives most probably from local sources, including Hg re-emitted from soil and a presumably scarce component taken up by the root system. A precise quantification of the different contributions would require the use of isotopic techniques (Gustin et al., 2022; Han et al., 2020; Pribil et al., 2020; Scanlon et al., 2020). Also, large knowledge gaps exist in understanding physiological and environmental controls of vegetation Hg uptake and transport within plants (Siwik et al., 2010; Zhou et al., 2021), not allowing to interpret differences between species Hg uptake (e.g. poplar, oaks and *Robinia* spp.) at the same sites. Anomalous Hg concentrations (93–738 μg/kg) in few tree samples are probably associated with very fine soil particles with high Hg concentrations trapped in the trees.

4.2. Implication for local management of spontaneous riparian vegetation

4.2.1. Biomass production and Hg emission potential and control of contaminated riverbanks soil erosion

The high level of resilience and productivity (fast regeneration and quick growth rate) of riparian tree species like poplars contributes to the rapid biomass accumulation of riparian vegetation, making these ecosystems of potential interest for biomass production for energy (Cartisano et al., 2013; Vaccari et al., 2022). For example, along a stretch of the Paglia River partly overlapping with that surveyed in our study, it was estimated that more than 70 ha of poplar dominated forests were naturally regenerated between 1989 and 2006 (Cartisano et al., 2013). Here, occasional harvesting of riparian trees to obtain biomass for energy production (e.g. wood chips used as a biofuel; wood for firewood) occur randomly, without selection of a specific species. Even residues derived from riverbanks habitat maintenance, mainly formed by riparian vegetation, can be used as a renewable biomass (Vaccari et al., 2022). Surely poplar trees, being the most abundant, would represent most of the harvested species, followed by the others. At the investigated sites we found *Robinia* trees cuttings with new tree regeneration, showing that also this species is harvested. Indeed, *R. pseudoacacia* is a fast-growing tree, and it is used for erosion control, amelioration, and reclamation of disturbed sites (Rahmonov et al., 2020; Vítková et al., 2017) and for biomass production in short-rotation energy plantations because of its high calorific potential and the high suckering capacity, which makes coppicing the most cost-effective management system (Sitzia et al., 2016).

Spontaneous *Populus*, *Robinia* as well *Quercus* trees, found along the Paglia riverbanks are of widely variable size and age, depending largely on those random cuttings. Because of the chaotic, continually changing distribution of spontaneous vegetation along the riverbanks, it is very difficult to quantify the total number of trees occurring in the investigated sites, nor their size distribution. It is beyond the scope of this contribution an accurate estimate of the total biomass of riparian trees along the investigated sites of the Paglia River; however, we estimated an order of magnitude based on a) the total area covered by riparian woods; b) an aboveground biomass of the riparian forest estimate of 88 tons/hectare (Mg/ha) calculated by Cartisano et al. (2013) along a stretch of the Paglia River. The area covered by riparian woods along the studied area calculated in GIS from the regional cartography provided by the Territorial and Environmental Information System of Tuscany (https://www.regione.toscana.it/-/geoscopio) and Lazio (https://dati.lazio.it), is about 1.8 km^2. Based on this area we obtain an order of 16,000 tons for the total riparian biomass, showing the potentiality of riverbank biomass as a sustainable resource for small-scale local energy production in the area.

Besides, biomass burning have shown to significantly contribute to the regional atmospheric Hg budget (Table 3) (e.g. Cinnirella et al., 2008; Engle et al., 2006; Pirrone et al., 2010; Melendez-Perez et al., 2014; Campos et al., 2015; Webster et al., 2016; Patel et al., 2019). For example, wildfires and prescribed burns in the United States release 19 to 64 $\times$ 10^6 g of Hg annually, representing between 13 and 42% of the estimated United States anthropogenic Hg flux of 150 $\times$ 10^6 g (Biswas et al., 2007). However, worldwide biomass burning is not well characterized as a source of Hg emissions (Friedli et al., 2009; Yang et al., 2018). Since extreme heat and drought, once relatively rare in Europe, are becoming increasingly common, wildfire risks are already critical in southern Europe and are projected to increase further (EEA - European Environmental Agency, 2024, European Pellet Council), estimated the potential Hg emissions in the case of a wildfire involving this Hg anomalous riparian area. Assuming conservatively that the average total Hg content of bole wood analyzed in our study is of 15.3 μg/kg (Table 1), by applying this value to the total estimated biomass (16,000 tons), riparian vegetation along the studied stretch (1.8 km^2) of the Paglia River store a total Hg mass of 0.24 kg, equivalent to about $1.4*10^{-3}$ kg Hg/ha. This estimate is made on the bole wood, which is only a part, albeit major, of the total biomass of the tree, known to contain the lowest Hg concentrations (Zhou et al., 2021). The other components (bark and leaves) typically have higher Hg contents (Yang et al., 2018; Zhou et al.,

Table 3
Summary of Hg emission (g/ha) from plant biomass burning during wildfires in other parts of the world.

Location	Burning source	Hg emission (g/ha)	Reference
United States	vegetal biomass	3.6–25.3	Biswas et al. (2007)
United States	vegetal biomass	5.5	Patel et al. (2019)
United States	vegetal biomass soil	0.9–7.8 1–30	Webster et al. (2016)
United States	vegetal biomass	2.2–4.9	Engle et al. (2006)
Brazil	vegetal biomass + soil	4.1 ± 1.4	Melendez-Perez et al. (2014)
Portugal	soil	1.0–1.1	Campos et al. (2015)

2021), making our estimate presumably a minimum value for the total Hg mass. Contribution to atmospheric Hg during a wildfire will be higher than our estimate because Hg will derive also from leaves, tree branches, barks, containing higher Hg content, as well as by burning of roots and litterfall (Biswas et al., 2007; Campos et al., 2015; Webster et al., 2016; Francisco-Lopez et al., 2022). However, wood represents the largest component of forest biomass, representing a large Hg pool, and an important contribution to the Hg budget in forests (Yang et al., 2018). Also, a more substantial contribution may come from the volatilization of Hg from soil. Previous studies in the MAMD (Fornasaro et al., 2022e; Delicato, 2021) estimated Hg storages in tree components and soil of about 1375 g/ha at Abbadia San Salvatore (1.5 km form the mine site), finding that the topsoil is the major reservoir for Hg (>90–95%). According to several studies (e.g. Biswas et al., 2007; Tuhý et al., 2020; Webster et al., 2016), an above-ground fire causes the release of Hg from a soil thickness in the order of some cm, depending on several factors, such as the nature of the soil, the type of aboveground vegetation, and the severity of the fire (reached temperature, e.g. Webster et al., 2016). In the investigated area the mass of Hg released from topsoil in case of a wildfire was calculated according to equation (1) (modified from Webster et al. (2016), supplementary material), linking the density of soil, the soil depth interested by the fire and Hg concentrations in soil. We assumed that a wildfire would release all Hg content (100 %) from the top 7 cm of soil that is mainly composed of litterfall based on a previous study in the Mt. Amiata area (Delicato, 2021; Fornasaro et al., 2022e). Also, we inferred that in the investigated area the depth interested by the fire has the same effective thickness and an average soil density of 1.3 g/cm^3, calculated from the relationship between organic carbon (OC %) and density (equation (2), Hossain et al., 2015, supplementary material). This estimate shows that about $4.8 * 10^3$ kg of Hg would be released from topsoil in the area (1.8 km^2) considering a homogeneous distribution of Hg in soils (29.7 mg/kg) corresponding to the average Hg concentrations at the 5 sites. These assumptions lead to an estimate of 27 kg Hg/ha, assuming uniform distribution of Hg concentrations and, ranging between 2 and 48 kg/ha based on minimum and maximum Hg concentrations in soils~~,~~ (Table 2). The range of Hg emissions would be more variable considering that the riparian areas is inside the segment of the Paglia River defined as "contaminated corridor" in Fornasaro et al. (2022c), where Hg concentrations in soils show high variability (0.1–186 mg/kg), and Hg is above 1 mg/kg (Italian limit for green area soils; D. Lgs 152/2006-Legislative Decree, 2006) in over 83 % of the river sediments and soils (Fornasaro et al., 2022c).

Consequently, management practices in Hg anomalous riparian areas should be implemented considering the economic and sustainable value of riparian trees for biomass production and should include an assessment of biomass and soil Hg content to estimate the potential Hg emissions into the atmosphere following wildfires. This will contribute to assess the Hg atmospheric budget and it will also serve to local authorities to implement fire risk assessments, suggesting appropriate safety measures to reduce Hg inhalation risks for local persons or in case of fireman's intervention during a wildfire or for the local population.

Also, in these peculiar sites, management plans should highlight the importance of riparian trees in limiting riverbanks soil erosion rates. Indeed, several authors (Dawson and Lewin, 2023 and reference therein) demonstrated that root systems, particularly the density of fine root systems, affect the stability and thus the erodibility of riverbanks and the substrate of riparian forests. In particular, the above-ground biomass strongly ameliorates the resistance to erosion of riverbanks under flood conditions. Along the Paglia river stretch, Pattelli et al. (2014) documented that flood events can erode and transport high masses of Hg, with up to 905 μg/kg of Hg found in overbank sediments after a major flood event in 2012. Colica et al. (2019) estimated a total mass of at least 60 tons of Hg stored along the Paglia fluvial terraces, only in the Tuscan stretch (thus excluding its Umbrian and Latium tract). Fornasaro et al. (2022a) showed that up to 40 kg/year of Hg are discharged by the Tiber River to the Mediterranean Sea at Rome, stressing that because of climate changes, more frequent localized short-term extreme weather events (e.g. high-frequency rainstorms, floods) in Southern Tuscany, will increase Hg fluxes toward the Mediterranean Sea, through the Paglia-Tiber River system. Riparian vegetation thus contributes to lowering the Hg fluxes, limiting riverbanks soil erosion during flooding, hindering Hg to reach the sea, where Hg may easily enter in the food chain through its methylation (Bargagli and Rota, 2024; Tada et al., 2023). As detailed for the Paglia River system, the protection from erosion of polluted riverbanks through the management of spontaneous vegetation is possibly the lesser evil, with negligible consequences for the quality of riparian biomasses to be used for energy production, provided the realization of adequate protection from wildfires. *Robinia pseudoacacia* species for example are suitable species for riverbank management, to prevent soil degradation, ~~and~~ to limit soil erosion (Băbău et al., 2021; Kou et al., 2016) and being also moderate to low accumulators of heavy metals (including, in this case, Hg). This approach, which may sound self-evident, is not so obvious in the reclamation strategies followed in mine reclamations in the past. As a local example, the Siele Hg mine, belonging to the MAMD district (Fig. 1), was the first Hg mine to undergo reclamation (1996–2001) at the worldwide scale (Fornasaro et al., 2022b and references therein). In this area remediation of stream sediments and overbanks downstream of the mine was not deemed necessary, although it was well known that during mining operations waste material was discharged into the stream. At the time of reclamation (Mining Italiana spa was owner of the mining concession), it was thought that any Hg-bearing sediment would be shortly washed away, so that a natural cleanup would occur. Conversely, the Siele River system has a low resilience and natural recovery will take many years, during which the area will remain an important source of Hg for the Paglia and Tiber River systems (Fornasaro et al., 2022b). The MAMD is only one example of a highly contaminated river catchment source of legacy mine pollution to the surrounding environment. Macklin and Thomas, (2023) estimated that more than 23 million people live in floodplains contaminated by heavy metals originating from mines, highlighting that long-term discharge of mining waste into rivers is far greater (almost 50 times) compared to the number directly affected by tailings dam failures. Development of tools including all the environmental compartments (aquatic, atmospheric, biological and vegetation) that can contribute to environmental management strategies are needed to prevent future contaminant dispersal. A wise management intervention in riparian areas should find a compromise between harvesting riparian trees for biomass, respecting their restoration time and limiting organic matter dispersal, and maintaining enough trees to make the most of their ecological functions (reduce the hydraulic risk, lower erosion and contaminant dispersion, trap Hg).

4.3. Wood chips and biofuel

Wood biomass represents a renewable and cost-effective energy resource (e.g., Al-Hamamre et al., 2017; Chandrasekaran et al., 2012). As said before, the occasional harvesting of riparian trees in the Paglia River banks is used for energy production and it is an important available residential and commercial source for space heating energy needs, in the form of wood chips or pellets. However, contaminant uptake by plants may result in environmental problems related to the combustion of contaminated wood products. The Hg concentration range in trees found in this study is comparable with literature values for commercial wood chips (species undefined). For instance, Rector et al. (2013) and Rimar et al. (2022) report values in the order of 1 μg/kg, for wood chips from Northeastern USA and Slovakia, i.e. at the lowest end of concentrations reported in this study. By contrast, Wiktor et al. (2017) report Hg values ranging from 60 to 295 μg/kg for wood chips from Poland, i.e. at the upper end of concentrations reported in this study. In many countries, the quality of solid biofuels is regulated by specific norms such as the US ASABE AD17225 (2018) and the European standard for wood pellets (EN 14961-2, 2011), followed by the international standard (ISO 17225). In the European market 80% of pellets for heating are ENplus certified, a quality certification program which follows the ISO 17225 norm (European Pellet Council. ENplus). According to the European EN ISO 17225 (2021) norm, for the best material (Grade A) certification of heavy metal contents is "not required as these classes of fuels are chemically untreated wood residues or from virgin material, which has been grown in uncontaminated land and therefore the likelihood of contamination is very low". The classification in grades means that solid biofuel is used either in commercial applications such as in households and small commercial and public sector buildings or in industrial applications (EN ISO 17225, 2021). "Typical values" of Hg for Grade A materials are in the range 20–50 μg/kg for virgin forest wood, and less than 30 μg/kg for poplars from short rotation coppice. The recommended limit for Hg in Grade B material (includes short rotation coppice from contaminated soil, wood from gardens and plantation, etc.) is 100 μg/kg. Mercury measured in trees along the Paglia River section are below this limit, and not far from "typical values" of Grade A material (Fig. 4). Therefore, Hg contents should have little to moderate impact on the commercial value of the locally harvested wood chips. However, the occasional occurrence of higher values (between 195 and 738 μg/kg) may suggest the opportunity of random tests to monitor the product quality. Given the increasing use of chips as a source of energy, this should be a general suggestion for the implementation of norms for wood chips production in areas with natural geogenic anomalies, where wood collected in forests considered as "virgin" (Grade A, EN ISO 17225, 2021) might contain metals.

5. Conclusions

Riparian trees and soils were investigated for their Hg contents along the riverbanks of the Paglia River (Tuscany, Italy), an emblematic case of non-remediable Hg-impacted catchment due to the historical mining activity of the Monte Amiata Hg district, the 3rd former Hg producer worldwide. Riparian vegetation, and specifically poplar, black locust, and oak, showed Hg contents in wood within the range of 0.7–59.9 μg/kg (average concentrations for all trees 15.3 μg/kg). In *Populus* trees Hg ranged between 2.4 and 59.9 μg/kg, in *Quercus* between 5.1 and 24.7 μg/kg, and in *R. pseudoacacia* between 0.7 and 32.5 μg/kg. Concentrations of Hg in soils varied from 2.2 to 52.8 mg/kg. Results showed that riparian vegetation acts as a sink of Hg along the Paglia riverbanks and in the studied segment may contain at least 0.24 kg of Hg. This estimate is presumably a minimum value of the total Hg mass stored in trees because it is based only on bole wood concentrations, not including barks, leaves, and branches.

In case of wildfires, Hg stored in trees ($1.4*10^{-3}$ kg Hg/ha) and in the topsoil (about 27 kg Hg/ha) will be a source of Hg^0 to the atmosphere, contributing to the Hg biogeochemical cycle and representing a risk to the surrounding environment (biota, human health, and animals). The occasional harvesting of riparian trees for energy production provides a wood chip material whose Hg content is basically compliant with European quality standards. Mercury concentrations in trees are below the recommended Hg limit (100 μg/kg) for good quality (Grade B) solid biofuels (European EN ISO 17225, 2021), thus posing little to moderate impact on the value of the locally harvested wood chips and to the potential health risk for Hg^0 emissions. Given the high Hg concentrations in riverbank soils, riparian vegetation along the Paglia River also represents an important tool to mitigate mechanical Hg dispersion in the aquatic environment, through stabilization of the riverbanks, decreasing the risk of potential methylation and bioaccumulation of Hg in the food chain. Controlling the erosion of contaminated overbank sediments along river stretches by means of riparian vegetation is probably the best pragmatic choice to minimize the transfer of heavy elements to the sea, especially with the increase of extreme events (floods, heavy rains) due to climate change. This strategy appears to be the lesser evil in the Paglia River system with the aim to preserve as much as possible the Mediterranean Sea, an environmental resource having a boundless value. In this context, in Hg-polluted and non-remediable riparian areas (because of huge costs), results from this research provide suggestions for the implementation of new future management practices. Riparian vegetation, often not considered as a priority in environmental river management, provides an important contribution to improve environmental quality. Management and restoration plans should consider riparian vegetation as a sustainable remediation tool, by integrating its known role in limiting erosion and contaminants dispersion in the watershed, with the use of biomass for energy production, providing additional economic benefit to local communities. The development of new management practices should include i) an assessment of riparian trees biomass, ii) a quantification of Hg stored in riparian trees and soils, to determine their capacity of trapping Hg from riverbanks, therefore helping in remediation of hg contaminated areas, and iii) an assessment of the potential Hg emissions to the atmosphere in case of fire and for its use as biomass for energy production, to determine the risk to the environment and human health. This assessment will help in finding the appropriate solutions, locally tailored, to reduce the potential risk of Hg release into the atmosphere occurring in Hg-anomalous areas during wildfires. Also, it will contribute to the implementation of regulations for wood chips production in areas with natural geogenic anomalies. Further research at a larger scale is essential to provide new information about the biogeochemical cycling of Hg (and other contaminants) and its behavior from soil to wood, to better include riparian vegetation as part of contaminated river basin management.

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CRediT authorship contribution statement

Guia Morelli: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Francesco Ciani:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Claudia Cocozza:** Writing – review & editing, Data curation. **Pilario Costagliola:** Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation, Funding acquisition, Data curation, Conceptualization. **Cesare Fagotti:** Supervision, Investigation, Funding acquisition. **Rossella Friani:** Methodology. **Pierfranco Lattanzi:** Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Rosarosa Manca:** Writing – review & editing, Investigation. **Alessio Monnanni:** Writing – review & editing, Investigation. **Alessia Nannoni:** Writing – review & editing, Investigation. **Valentina Rimondi:** Writing – review & editing, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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