

Article

Distribution of Thallium in Sediments of the Fiora River Catchment, Central Italy: Implications for Its Sources

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Abstract

Previous studies documented the contribution of toxic elements (Hg, As, and Sb) from the dismissed Monte Amiata Mining District (Italy), the third largest Hg producer worldwide, to the Mediterranean Sea. Another highly toxic element, thallium (Tl), received less attention. Here we report a reconnaissance study of the spatial variability of Tl content in stream sediments across the Fiora River catchment, which drains part of the Hg and Sb mining districts. Thallium contents are comparatively low (≤ 0.4 mg/kg) in sediments of creeks directly draining the mining areas, whereas they increase up to 2 mg/kg in the catchment section that drains the Vulsini ultrapotassic volcanic province, where no known mineral deposits occur. Results suggest that Hg and Sb deposits cannot be the only Tl source in the catchment. The most likely alternative/additional candidate are the high-K volcanic rocks. Although no specific data for the Vulsini district exist, a distinct Tl geochemical anomaly linked to the Latium volcanic province is present. The total Tl mass contained in sediments discharged yearly into the Mediterranean Sea from the Fiora River is estimated in the order of 0.1 t. This reconnaissance study indicates a non-negligible potential release of Tl from the mining districts and volcanic catchments in Central Italy and suggests the opportunity of further investigation on Tl distribution and speciation in the area.

Keywords: Thallium; Fiora River; pollution; stream sediments; contaminant hydrology; Vulsini volcanic province



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1. Introduction

The study of pollutant distribution in the aquatic system is fundamental to protect the water resource and the environment. For this purpose, stream sediment chemistry is often investigated, because it reflects the spatial and temporal distribution of contaminants in waters [1–3]. Moreover, stream sediment pollution poses significant threats to water quality, aquatic ecosystems, and human health [4–16]. Metal(loid)s in soils and stream sediments derive from either geogenic sources (i.e., parent material) or anthropogenic contamination [17]. The assessment of the natural geochemical background for metals in sediments is critical to evaluate the contribution of human activities to the total metal budget of an environmental system [18]. Among human activities, mining releases huge

volumes of wastes that are polluted by toxic metal(loid)s and are then redistributed across the catchment through runoff. Consequently, the dispersion of a specific toxic element in a mine-impacted riverine system could be caused by multiple sources, both anthropogenic and geogenic.

Previous studies demonstrated that, in the Monte Amiata Mercury District (MAMD; central Italy), heavily polluted metallurgical wastes dumped around the former mining sites were mobilized by runoff, spreading the pollution downstream and ultimately into the Mediterranean Sea [18–30]. These studies were mostly focused on Hg and subordinately dealt with As and Sb. Thallium received comparatively little attention, with only a few studies restricted to the Apuan mining district in Northern Tuscany ([13,31] and references therein). The only data available for the Southern Tuscany metalliferous province are limited to soil data by [32] and some mineral analyses by [31] (see details in the Discussion).

The Fiora River catchment drains the southern portion of the MAMD and a small portion of the Southern Tuscany Sb district. Recent findings suggest a major contribution of As, Hg, and Sb from the MAMD, whereas the contribution from the Sb district is marginal [30]. Samples collected in the Fiora River catchment for that study [30] are here investigated for Tl. The data obtained are discussed to (1) study the spatial variability of Tl in stream sediments collected across the Fiora River catchment, (2) give a preliminary assessment of the source(s) of this metal, and (3) estimate yearly fluxes of Tl to the Tyrrhenian Sea to evaluate the contribution of the FR to the toxic elements budget of the Mediterranean. This is the first investigation on Tl dispersion across a catchment of the Southern Tuscany metalliferous province, which aims to open further investigation in the area.

2. Background Information

2.1. Thallium Geochemistry and Toxicology

Thallium is a fairly rare metal, with an average content in the upper continental crust of 0.49–0.75 mg/kg [33–35]. It shows both chalcophile and lithophile geochemical affinities, and it is therefore concentrated either in epithermal sulfide deposits, where it may form proper minerals, but more often occurs as a trace element in sulfides such as chalcopyrite, sphalerite, marcasite, and pyrite or in potassium minerals (alkali feldspar and micas) of igneous rocks [36–40]. Industrial coal combustion and mine/industrial waste erosion are the primary anthropogenic sources, whereas mechanical erosion of ore deposits and volcanic rocks are considered potential natural sources of Tl [41–44]. Thallium has no known biological functions and it is in fact highly toxic, acting as a cumulative poison and a neurotoxin [45,46]. The toxicity arises from the similar ionic radii of Tl^+ and K^+ causing interference with vital potassium-dependent processes, substitution of potassium in the (Na^+/K^+) -ATPase, as well as a high affinity for sulfhydryl groups from proteins and other biomolecules [47]. Thallium is absorbed by humans through skin and mucous membranes and its biological half-life in man is 3–8 days ([41] and references therein). Currently, chronic intoxication by Tl is a global concern, as several cases of water contamination have been registered [48–50]. On the other hand, Tl has several applications is listed among the energy-critical elements by the European Union (European COST Action TD1407: Network on Technology-Critical Elements; [51]). This element is crucial for strategic industrial sectors and new technologies, such as renewable energy, electric mobility, defense, aerospace, and digital technologies. Approximately 70% of Tl production is used in electronic devices [52].

2.2. The Monte Amiata Mining District

The Mt. Amiata Mining District (MAMD, Southern Tuscany, Italy) was the third largest Hg producer worldwide, with a cumulative production of more than 100,000 tons of Hg [53–55]. The mining activity started during the Etruscan period for cinnabar ex-

exploitation; the Morone mine was the most exploited site during the pre-industrial era [53]. The most intense period of Hg exploitation occurred from the 1870s to 1982, when the activity was dismissed permanently. Forty-two former mining sites are present in the MAMD (Figure 1), the Abbadia San Salvatore mine (ASSM) being the most important one, followed by the Abetina-Solforate-Rosselli-Schwarzenberg (ASRS) and the Morone mining sites [53,56]. Smelting was conducted on site at the main mines; ASSM and Siele were the most important smelting centers. South of the MAMD, the Sb metallogenic province extends and, here, Sb extraction was active between the beginning of the 19th century and 1980 (Figure 1).

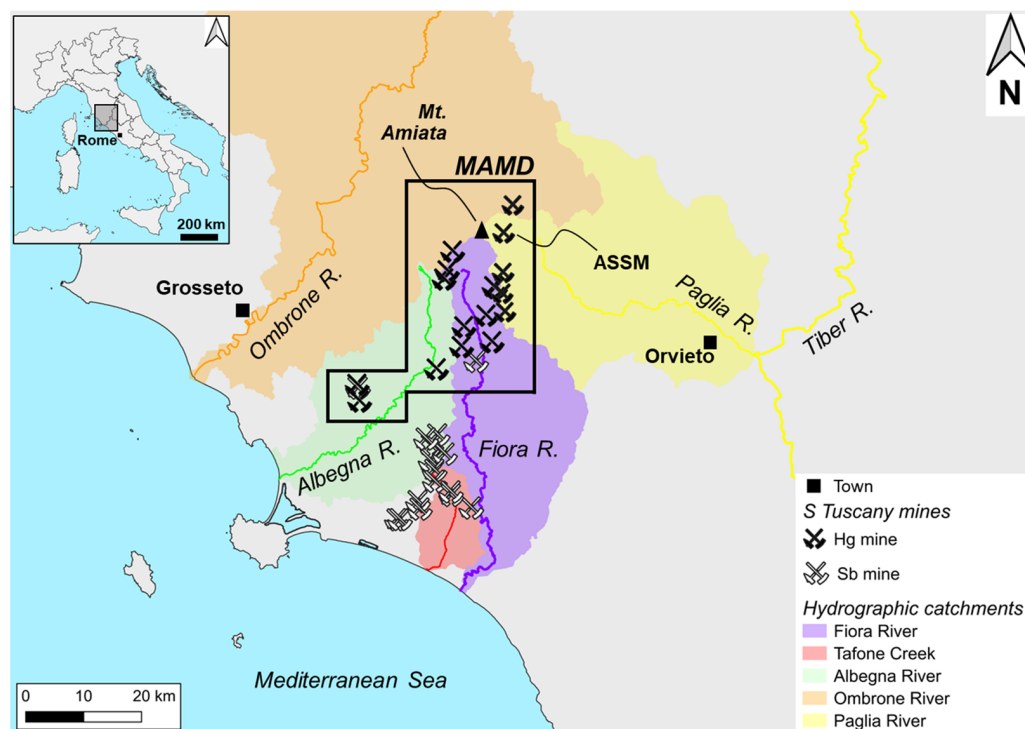


Figure 1. River catchments in Southern Tuscany Hg-Sb province. The main abandoned Hg mines of the Mt. Amiata Mining District (MAMD) are delimited by the black polygon. The Fiora River catchment is highlighted in purple. Modified after [30].

3. Study Area: The Fiora River Catchment

3.1. Geology

The Mt. Amiata Mining District (MAMD, Figure 1) covers an area of about 400 km² and belongs to the Tuscan metalliferous province [57,58]. The area is characterized by the Quaternary volcanic edifice of Mt. Amiata (1738 m asl). The geological evolution of the area is related to the Tertiary Apennines orogeny and the following post-collisional phases [59,60]. The volcanic products were emplaced over, from bottom to top, the Paleozoic basement, Tuscan units (Triassic limestones and Cretaceous–Oligocene terrigenous formations), Ligurian–Subligurian units (Jurassic–Oligocene), and Neogene sediments (Figure 2a; [61]). Ore deposits originated in the Mt. Amiata surroundings due to hydrothermal activity accompanying the cooling of magmatic bodies that were emplaced during Pliocene–Quaternary [54,62]; hydrothermal circulation is still ongoing [63,64]. Cinnabar (α -HgS) was the sole ore mineral, other Hg phases being rare. Pyrite and marcasite (FeS_2) are ubiquitous, whereas realgar (As_4S_4) and orpiment (As_2S_3) are common; stibnite (Sb_2S_3) is sparse [54]. The Fiora catchment is mostly made up of volcanic (43%) and sedimentary clastic rocks (24%).

The upstream section of the catchment developed over the eruptive products of Mt. Amiata; then, from Santa Fiora to the Monticchio Creek (“r” in Figure 2; Table 1) confluence, the river flows over the clastic rocks of the Tuscan and Ligurian nappes. The mid and downstream sections of the catchment developed over the Latera–Bolsena volcanic rocks (Vulsini volcanic province), travertine deposits, and recent alluvial sediments (Figure 2a). The Vulsini volcanic province belongs to the so-called potassic and ultra-potassic belt of Central Italy running from northern Latium to the Neapolitan area. The belt is mainly composed of undersaturated alkaline rocks that are rich in both K_2O and Na_2O [65].

Table 1. List of the Fiora River main tributaries from upstream to downstream. The number of samples collected in 2022 and the presence of Hg/Sb mineralization in each tributary sub-catchment are also reported. Modified after [30].

Tributary Label	Tributary Name	Sub-Catchment	Mine/Mineralization in the Sub-Basin	Mine Site (Mine Code)	Ore	Samples
a	Ontani creek	Ontani	Yes	Bagnore (1)	Hg	1
b	Famelico cr.	Ontani	No	-	-	1
c	Putrido cr.	Ontani	Yes	Antee tunnel (2)	Hg	1
d	Formica cr.	Formica	Yes	Mt. Labro (3)	Hg	1
e	Cadone cr.	Cadone	No	-	-	-
f	Scabbia cr.	Scabbia	Yes	ASRS (4,5)	Hg	2
g	Abetosio cr.	Scabbia	No	-	-	1
h	Rico secco cr.	Scabbia	Yes (mineralization)	-	-	1
i	Solforate cr.	Scabbia	Yes	ASRS (4,5)	Hg	3
j	Salto cr.	Scabbia	No	-	-	1
k	Lascone cr.	Lascone	No	-	-	-
l	La Solfarata cr.	La Carminata	Yes (mineralization)	-	-	1
m	La Carminata cr.	La Carminata	Yes (mineralization)	-	-	2
n	La Canala cr.	La Canala	Yes	Morone (6)	Hg	3
o	Maestrino cr.	Maestrino	Yes	Cortevvecchia (7)	Hg	2
p	Reto cr.	Reto	Yes	Reto (8)	Hg	3
q	Rigo cr.	Rigo	Yes	Cortevvecchia (7)	Hg	2
r	Monticchio cr.	Monticchio	Yes	S. Martino sul Fiora (10)	Sb	1
s	Segno cr.	Segno	No	-	-	1
t	Calesina cr.	Calesina	No	-	-	1
u	Fuliggine cr.	Fuliggine	Yes	Catabbio (9)	Hg	2
v	Lente stream	Lente	No	-	-	1
w	Procchio cr.	Lente	No	-	-	1
x	La Nova cr.	La Nova	No	-	-	-
y	Gamberaio cr.	Gamberaio	Yes (mineralization)	Podere Pietricci (10)	Sb	-
z	Olpeta stream	Olpeta	No	-	-	1
α	Gricciano cr.	Gricciano	Yes (mineralization)	-	-	-
β	Pozzatelli cr.	Pozzatelli	Yes	Montauto (12)	Sb	-
δ	Timone stream	Timone	No	-	-	1

3.2. Geomorphology and Hydrology

The Fiora River (FR) catchment covers an area of 826.9 km²; the main river course flows with a N–S direction for 84 km from the confluence of the Ontani, Putrido, and Cadone creeks (“a”, “c”, and “e” in Figure 2b and Table 1), on the southern slope of Mt. Amiata to the Mediterranean Sea, in the vicinity of Montalto di Castro (Figure 2b). The Fiora catchment shares parts of its watershed with all the remaining three MAMD catchments (Paglia, Ombrone, and Albegna; Figure 1). Yearly discharge at the Fiora River mouth varies between 3 m³/s (summer) and 18 m³/s (winter), with a mean value of 6.3 m³/s [66].

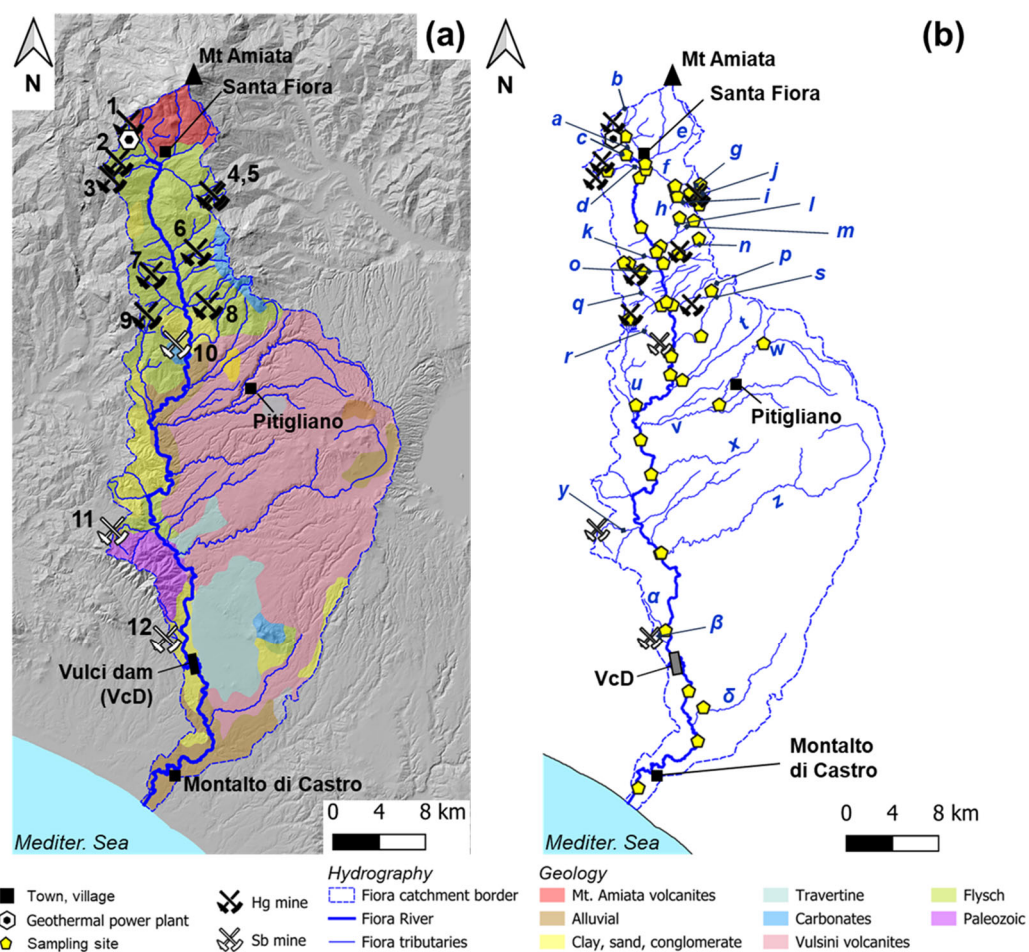


Figure 2. (a) Map of the outcropping lithologies across the Fiora River (FR) catchment (modified after [30,67]). (b) Catchment hydrography of the FR and sampling site locations (yellow pentagons). The labels of FR main tributaries and Southern Tuscany former mines in the catchment are explained in Table 1.

The Fiora catchment is characterized by an asymmetrical relief; the western side of the catchment shows steep slopes and short, torrential tributaries, whereas the eastern side of the catchment exhibits well-developed sub-catchments with a smoother morphology. The catchment has a soil-use percentage for anthropic activities of 65.3%, with former mining areas covering 0.12% [68]. The FR main course was altered in 1923 by a dam (Vulci Dam) built close to the Vulci archeological site for hydroelectric purposes (Figure 2). The lake upstream of the dam experienced severe silting, which forced the managing authority to adopt clean-up measures in 2016. The silting was caused by three factors: the nature of the sediment supply, the quaternary regional uplift, which led to the ongoing rejuvenation of the catchment, and the frequent occurrence of flooding events along the FR [69].

3.3. Mining in the Fiora River Catchment

Eleven dismissed mining and smelting sites are present in the upstream part of the Fiora River (FR) catchment (Figures 1 and 2; Table 1), including the second (ASRS) and the third (Morone) most important Hg production centers of the MAMD, which accounted for 1/3 of the total Hg production of the district. The other sites were of lower importance due to low Hg grades in the local orebodies [53,56]. The catchment receives runoff also from the Montauto mining site (“11” in Figure 2) and possibly from the Podere Pietricci site (“12” in Figure 2) belonging to the Southern Tuscany Sb mineralized district [70–72]. The environmental impact of the mine sites on the Fiora River catchment was observed for

some trace metals (Hg, Sb, and As) in a previous study, showing the role of the river in the redistribution of contaminants along the catchment [30]. Mass load estimations revealed that at least 0.4, 2.2, and 1.8 t/y of Hg, As, and Sb, respectively, could be released into the Mediterranean Sea [30].

4. Materials and Methods

Stream samples were collected in 2022 along the FR main course from the source to the river mouth, as well as on its active tributaries. The sediments were collected in plastic bags with a Teflon spoon in the first 5–10 cm layer in riffles and pools along the active watercourse. All samples are composite of 5 subsamples collected within 5 m². In total, 15 samples were collected along the FR main stretch; 35 samples were collected in the FR tributaries. For each mine-impacted tributary, at least two samples were collected, respectively, upstream and downstream of the mining site (Table 1). For secondary tributaries (i.e., less than 3 km long and not draining mining areas), one sample was collected immediately upstream of the confluence in the FR.

Sample preparation and analysis were carried out in the ARPAT laboratory in Siena. The samples were air dried at 20–25 °C, homogenized, and sieved with a 2 mm sieve to remove the gravel fraction, according to the Italian national guidelines [73]. Then, the samples were pulverized with a rotating agate ball mortar to less than 0.063 mm fraction. The sediment powders were digested by inverse aqua regia in a microwave oven prior to analysis [74]. Total Tl concentrations were analyzed following the EPA 6020B method [75]. The analyses were carried out by means of an ICP-MS IcapQ Thermo-Fisher (Thermo Fisher Scientific Inc., Waltham, MA, USA) in CCT mode (KEDS). The laboratory uses limit of quantification (LOQ, 0.1 mg/kg for Tl) instead of the LOD, assumed from the first readable point in the calibration curve and checked at the beginning of each analytical run by means of referenced certified material (CRM052 Trace Metals—Loamy Clay 1). The laboratory is subjected to periodical quality checks by an independent organization (Accredia, Rome, Italy) according to the standard ISO/IEC 17025 [76], and it takes part in the SNPA interlaboratory network for cross-checking. The overall analytical precision of the method is <10%, as determined by replicate analyses of different aliquots of the same bulk sample.

The total Tl fluxes (yearly mass loads) through the Vulci Dam over almost a century (from 1923 to 2012) were calculated based on data in the ENEL technical report for the Vulci Dam renovation [69]. Specifically, the ENEL report provides data that allow calculation of the total sediment mass accumulated in the reservoir. This sediment mass is divided by 89 (the years elapsed between 1923 and 2012) to obtain an estimate of the yearly mass of transported sediments. By multiplying the yearly mass load by the median Tl concentration in stream sediments across the catchment (0.2 mg/kg), an estimate of the yearly Tl flux is obtained. Further details for the mass load calculation can be found in Nannoni et al. [30].

The geoaccumulation index (I_{geo} [18,77,78]) for Tl was calculated across the catchment. This index provides information about the degree of anthropogenic enrichment of an element by comparison with its natural background levels. The index is calculated as follows:

$$I_{geo} = \ln [C_n / (1.5 \times B_n)],$$

where C_n is the concentration of the element n in the sample and B_n is the natural background of the same element. The natural background for Tl was chosen as the median (1.95 mg/kg) of the concentration range found in the stream sediments of the Southern Tuscany–Northern Latium area, as calculated by [77]. This value was chosen because the whole of Central Italy has a Tl anomaly and a local natural background is to be preferred with respect to a national/European-scale value.

5. Results

Overall, Tl concentration varied between <0.1 and 2 mg/kg (Supplementary Materials) in the stream sediments of the FR catchment, with mean and median values of 0.23 and 0.42 mg/kg, respectively. Thallium concentration along the FR main course was <0.3 mg/kg in the upstream stretch (ca. 30 km from the river mouth), from Santa Fiora down to the confluence of the Lente stream (“v”, Figures 3 and 4).

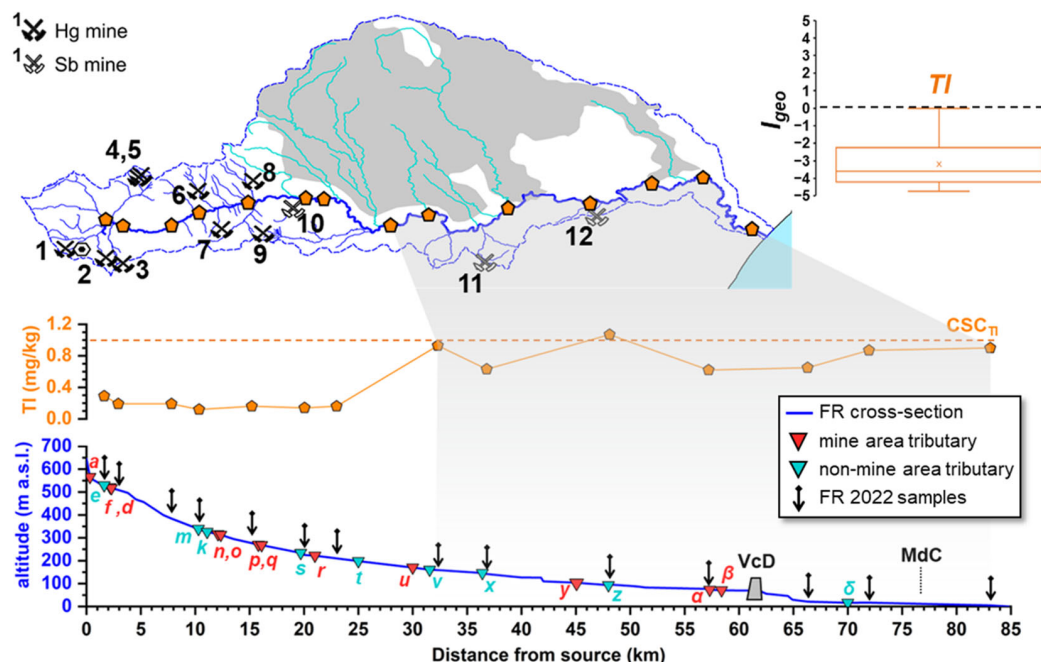


Figure 3. Bottom plot: elevation profile of the FR main stretch; the confluences of tributaries draining mining and non-mining areas are highlighted by reversed red and cyan triangles, respectively. Letters in red and cyan (a to δ) refer to the FR tributaries listed in Table 1. Mid-plot: distribution of Tl in 2022 along the FR main stretch, from the source to the mouth (distance in km shown in x-axis of the bottom plot). Top-left map: sampling sites, mines (1 to 12 as reported in Table 1), and Vulsini volcanites outcrops (in dark grey) location in the FR catchment. Top-right: boxplot of the I_{geo} index variability for Tl across the FR main stretch., VcD = Vulci Dam, MdC = Montalto di Castro village, CSC_{Tl} = Italian concentration threshold of Tl for public soils.

From the latter tributary confluence to FR mouth, Tl increased between 0.62 and 1.07 mg/kg, with a median value of 0.87 mg/kg (Figure 3). The highest concentration along the main stretch was found after the confluence of the Olpetta stream (“z”), ca. 50 km from the river mouth.

Thallium varied between 0.13 (Solforate cr., “i”) and 0.58 mg/kg (Famelico cr., “b”) in the upstream tributaries (Figure 4a). In the mid-section of the catchment, Tl ranged between <0.1 and 0.49 mg/kg along the tributaries that drain former mining sites, whereas creeks from the Latera–Bolsena volcanic area showed Tl concentrations between 0.42 and 2 mg/kg (“s” to “ δ ”, Figure 4b), with a median value of 1.12 mg/kg, i.e., exceeding the Italian concentration threshold for public green soils (“CSC”, 1 mg/kg; no threshold is defined for stream sediments in the Italian regulation [73]). Thallium varied between 0.13 (Solforate cr., “i”) and 0.58 mg/kg (Famelico cr., “b”) in the upstream tributaries (Figure 4a). In the mid-section of the catchment, Tl ranged between <0.1 and 0.49 mg/kg along the tributaries that drain former mining sites, whereas creeks from the Latera–Bolsena volcanic area showed Tl concentrations between 0.42 and 2 mg/kg (“s” to “ δ ”, Figure 4b), with a median value of 1.12 mg/kg, i.e., exceeding the CSC.

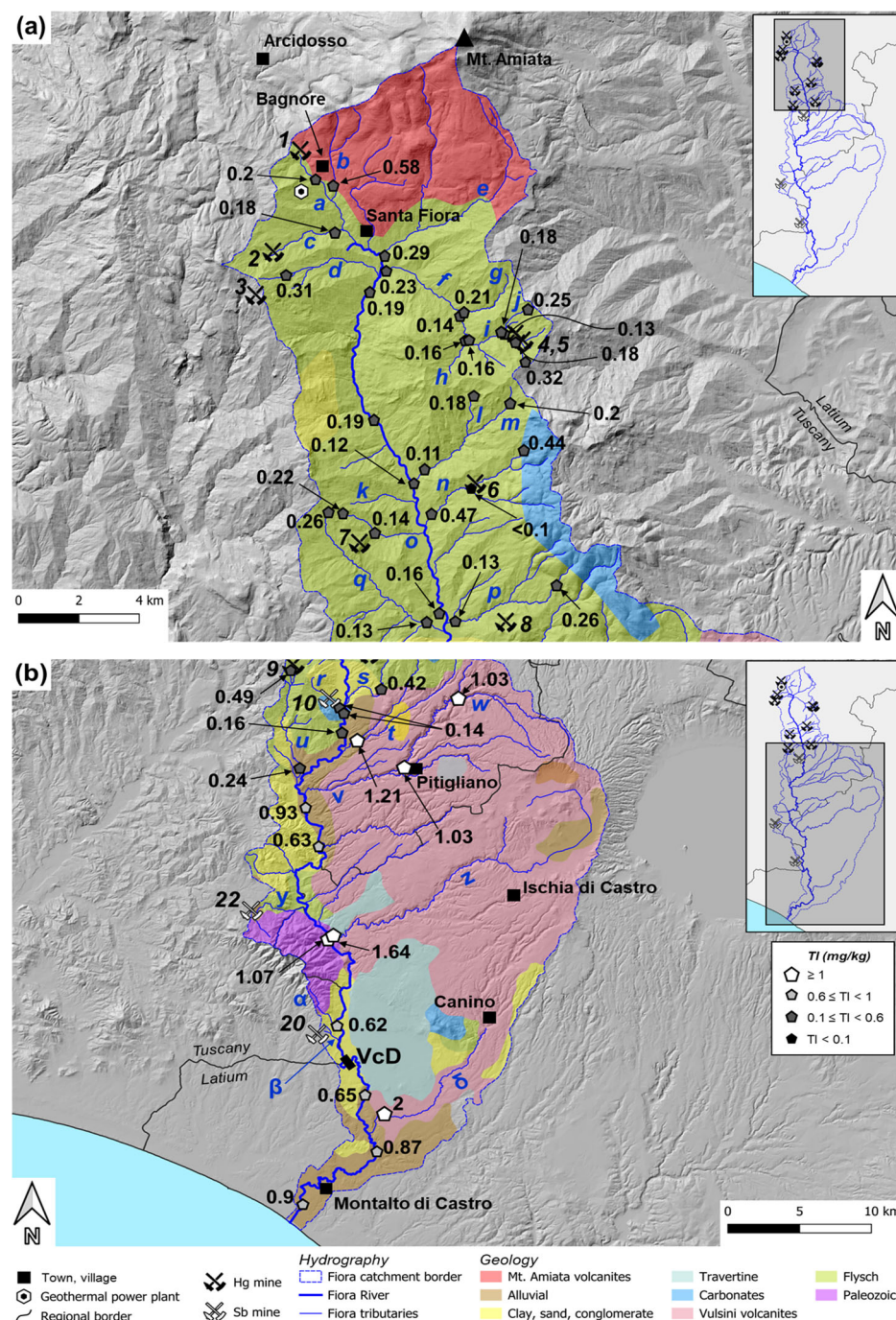


Figure 4. Spatial distribution of Tl concentration in stream sediments collected in 2022 across the FR catchment (a) in the first 20 km from the source and (b) from 20 km to the outflow. Labels that refer to the FR tributaries and MAMD mines are listed in Table 1, VcD = Vulci Dam.

Thallium concentration in the FR stream sediments was compared with Hg, Sb, and As concentrations in the same samples measured by [30]. The Pearson's correlation coefficient was always below 0.2 and the p -values ($\gg 0.05$) indicate no significant statistical correlation with the three elements (Figure 5).

The I_{geo} index varied between -4.7 and -0.5 across the catchment, with a median value of -3.6 (Table S1, Supplementary Materials). The index was always below 0, which corresponds to the “uncontaminated” class (i.e., with no anthropic inputs [18,77]).

Based on the total mass of sediments in the Vulci Dam and the median concentration of Tl in the whole catchment (0.2 mg/kg), it is estimated that the potential Tl flux discharged

by the Fiora River into the Mediterranean Sea is in the order of 0.1 t/y. This is a non-negligible amount and suggests the opportunity of additional studies on the sources and transport of this metal.

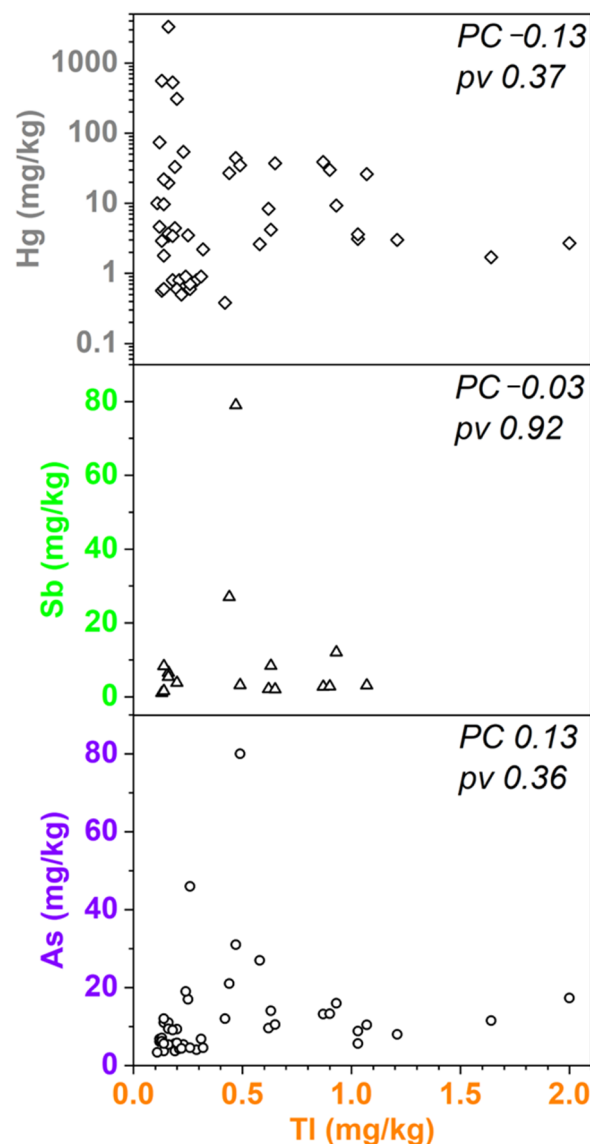


Figure 5. Comparison between Tl concentration in FR stream sediments and Hg, Sb, and As concentrations found in the same samples by [30]. Pearson correlation coefficient (PC) and the p -value (pv) are reported.

6. Discussion

Thallium values in this study were below the CSC (1 mg/kg [73]) in most of the FR catchment, with a mean value of 0.43 mg/kg, which is in the same range as the Tl concentration reported for the Earth's crust (0.49–0.75 mg/kg [33–35]) and the mean value for European stream sediments (0.477 mg/kg [79]). A national-scale assessment showed that Tl ranged between 0.01 and 5.62 mg/kg in Italian stream sediments, with a median value of 0.37 mg/kg [79]. The most anomalous (>2 mg/kg) concentrations in stream sediments are found in (1) the Latium volcanic area [79]; (2) near the border with Austria and Slovenia [79,80], in spatial association to the former Raibl Pb-Zn mine; and (3) in the streams draining the orebodies of the Apuan Alps in northern Tuscany [13,31]. Therefore, the Tl median value for the FR was slightly higher than the national value but lower than the European one. Thallium concentrations above the CSC were observed by [32] in

several Southern Tuscany soils, including both soils around mining areas (reported range: 1.6–6.1 mg/kg) and soils developed over acid to intermediate magmatic rocks (reported range: 1.8–5.7 mg/kg). At the national scale, Tl in soils (median value: 0.75 mg/kg [79]) exceeds the CSC in several areas. Again, the highest values (>2 mg/kg, up to 6.1 mg/kg) occur in the Latium–Campanian volcanic areas [79].

Thallium showed an interesting trend across the FR catchment. In the sectors draining the mines, Tl contents are comparatively low, whereas the highest concentrations (up to 2 mg/kg, i.e., above the CSC) were found in the tributaries that drain the high-K volcanic rocks cropping out in the Latera–Bolsena area, which is part of the Vulsini volcanic province [65,80–82], and downstream of their confluence in the FR. Moreover, if Tl contents are plotted against As, Hg, and Sb contents in the same samples (Figure 5), no significant correlation is observed ($p > 0.05$). Therefore, the former Hg–Sb mines cannot represent the only source of Tl in the catchment. Pyrite/marcasite, a common source of Tl [43], are frequent accessory phases in the ores of Morone, Reto, and S. Martino sul Fiora mines [83]. However, no data are available on their Tl content, except for a single analysis by [31] of marcasite from the Bagnore mine in the northernmost section of the Fiora River catchment (Figures 1 and 2). This sample returned a comparatively low Tl concentration (0.11 mg/kg). Higher concentrations of Tl were reported by [31] in marcasite/pyrite samples from the other catchments that drain the MAMD (201, 0.7–252, and 24 mg/kg in the Orcia, Paglia, and Albegna catchments, respectively); an even higher (3880 mg/kg) value was reported in a single sample from the Tafone Sb mine (drained by the Tafone creek, flowing directly to the Tyrrhenian Sea). Recent studies showed that a Tl fraction can be dissolved and then scavenged by the Fe–Mn oxide fraction close to sulfide mine areas, but most of the element is found in the residual fraction, particularly in stream sediments (e.g., [84,85]). Moreover, Tl-rich acid mine drainage waters (AMD) were found directly at the pollution source, e.g., acidic seeps and pools linked to mine workings, tailings piles, or mineralization outcrops. Conversely, runoff waters flowing through mining areas are usually depleted in Tl compared to AMD waters due to scavenging ([40] and references therein, [86]). This process should lead to a Tl enrichment in stream sediments with respect to water downstream of mining areas of sulfide ores. The low Tl grade in the local sulfide ores in the upstream section of the Fiora River catchment and, consequently, the low availability of Tl for weathering processes might explain the low Tl enrichment in the upstream Fiora sediments. It is, however, apparent that additional data (e.g., Tl speciation) are required to ascertain all the processes involved in Tl dispersion in the area.

The spatial correlation of high-Tl sediments collected in the FR catchment with sectors draining the Vulsini ultrapotassic volcanic province [65,80–82], where no known mineral deposits occur, suggests these magmatic rocks as the most likely additional/alternative source. High-K rocks may contain non-negligible Tl amounts because of the similar ionic radii of Tl^+ and K^+ [87]. Potassic and ultrapotassic magmatic rocks undergo Tl enrichment mostly through magmatic evolution, as demonstrated for several magmatic districts (e.g., [87] and references therein, [88]). In general, Tl behaves as an incompatible element and, therefore, is more concentrated in felsic magmas than in mafic ones (e.g., [87] and references therein); the average Tl concentration in 18 felsic rocks analyzed by [86] is 4.63 mg/kg. Biotite and K-feldspar are the typical Tl-bearing phases [87]; however, in silica-undersaturated rocks, leucite may be the main Tl host [89]. Consequently, these rocks can be a preferential, primary source of Tl. In the study area, weathering of K-silicates as a Tl source would be in agreement with data from another Italian ultrapotassic volcanic province, Roccamonfina (Northern Campania), where the groundwater is not enriched in Tl despite its availability due to weathering of high-K volcanic rocks, because it is scavenged by Fe- and Mn-bearing sediments [90]. However, no data of the Tl content of the ultrapotassic rocks

cropping out in our study area are available. South of the study area (40 km), in the Tolfa volcanic province, Tl concentrations up to 2.7 mg/kg were measured in unaltered acidic volcanic rocks, whereas 28 mg/kg and 74 mg/kg were found in pyrite and iron gossan, respectively [89]. High Tl concentrations (from 0.05 to 15 mg/kg) were found by [91] in the stream sediments of the Mignone River catchment, which partially developed over the volcanic products of the Tolfa and Sabatini districts, 20 km SE of the study area. However, those authors did not discuss Tl sources and distribution in the Mignone catchment.

In summary, Tl distribution in the Fiora River catchment seems to partly reflect the dual source of this element observed at the global scale. We already mentioned the Italian examples of Tl dispersion from sulfide mines [13,31,92]. Regarding European sulfide ores, the abandoned mine wastes near the Verdugal and La Mónica arsenopyrite–pyrite deposits (N-NW of Madrid, Spain) caused the pollution of surrounding soils and stream sediments (Tl up to 2.65 mg/kg [41]). Contamination was related to the physical alteration of mineralized rocks, natural erosion, and later pedogenic processes, with Tl bound to the residual silicate fraction [41]. The As-Sb-Tl hydrothermal ore of Allchar, Macedonia, is classified as a large reserve for Tl (over 500 t). Active hydrothermal alteration of the orebodies resulted in widespread Tl pollution in soils (range = 0.11–20,000 mg/kg, median = 5.2 mg/kg) and stream sediments (range = 0.78–25 mg/kg, median = 17 mg/kg for the samples collected downstream of the alteration zone [93]), whereas mining activity had moderate consequences for Tl contamination (mining was locally important only for Sb [93]). The stream sediments collected in the Pb-Zn sulfide Silesian district (Poland) showed Tl concentrations ranging from 1.49 to 147 mg/kg in the vicinity of the processing area; the element is preferentially associated with the oxidizable fraction, whereas the residual fraction controls Tl concentration in local soils [36,41]. Mineral processing was recognized as the primary cause of Tl enrichment in the district, followed by the weathering of outcropping ores [36]. At the global scale, the most prominent example is the peculiar Tl-rich sulfide deposit of Lanmuchang, China; stream sediments in the affected area have Tl contents as high as 72 mg/kg; pollution is related to both mining activity and natural weathering of Tl-rich minerals [94]. The Western Pearl River Basin (China) hosts one of the world's largest pyrite ore, and smelting is carried out onsite. Thallium concentrations up to 17.3 mg/kg were found in the stream sediments that were collected in the first 5 km downstream of the mine and their connection with mining activity was confirmed (the local natural background concentration is 0.55 mg/kg [37,95]). Moreover, most Tl in the stream sediments was associated primarily with the residual fraction (>65%) and secondarily with the Fe-Mn fraction, indicating that the migration of Tl from these sediments is weak [37,95]. A similar low mobility of Tl is reported for stream sediments near a sulfide metal mine in the UK [96].

A deeper understanding of Tl distribution in the Fiora River catchment would require specific studies of Tl abundance and speciation in mines, sediments, and magmatic rocks. Studies of Tl speciation would be crucial also to determine the bioavailability of the metal and its potential environmental and health impact.

Therefore, the results of this study suggest the opportunity for further investigation on the occurrence and potential Tl release from catchments draining the MAMD and/or high-K magmatic rocks. Thallium pollution should be addressed carefully, since it is one of the most toxic metals and it may cause more severe acute and chronic poisoning effects than Hg, Pb, Cd, and Zn for human health [97,98]. In fact, it is easily transferred from the geosphere to the biosphere due to Tl^+ affinity with K^+ [42,99,100].

The estimated particle-bound Tl mass loads released by the Fiora River (0.1 t/y) are similar to the amount (0.14 t/y) discharged in the Atlantic Ocean by the Rio Tinto River, draining the well-known mining district of the Iberian Pyrite belt, SW Spain [101]. A total

budget of 2.7 t/y was estimated for particle-bound Tl discharged in the Bohai Bay (N China) by multiple rivers; such input was related primarily to natural and secondarily to anthropogenic sources [102]. However, it should be noted that the Tl fluxes from the FR could be even higher, considering that sediment removal operations were carried out after the building of the Vulci Dam. The flux cannot be compared with other catchments of the MAMD, because no data are available at present. Further investigations are required to assess the total Tl flux from the MAMD and the Sb district; the Tafone Creek and the Albegna River drain Sb ores that contain non-negligible amounts of Tl, which could contribute to the Mediterranean Tl budget. Additionally, the Paglia River drains part of the MAMD and a part of the Latium high-K volcanic rocks in its downstream section; therefore, its contribution to Tl discharge to the Mediterranean basin cannot be ruled out at this stage.

7. Conclusions

The present study revealed that the Fiora River catchment (Tuscany, Italy) represents a non-negligible contributor to the Tl budget of the Mediterranean Sea. In sediments of creeks draining the mining areas of the dismissed Hg and Sb mine districts, Tl varied between 0.1 and 0.4 mg/kg. However, Tl distribution does not match that of other toxic elements such as Hg, As, and Sb, whose diffusion was attributed by previous studies to the past mining activities. The highest values (up to 2 mg/kg) were found in the tributaries which drain the Vulsini volcanic province, suggesting high-K magmatic rocks as an additional/alternative source of this metal in the catchment.

A preliminary estimation of Tl mass loads indicates that up to 0.1 t/y could be discharged into the Mediterranean Sea from the Fiora River catchment. This figure is presumably just a small part of a possibly much larger phenomenon. A regional-scale budget should include other catchments draining other Hg and Sb mines, where Tl could be more abundant, and/or high-K magmatic rocks. Consequently, further investigation should be carried out to (1) clarify the Tl mineralogical speciation in the source(s) and in the sediments to make inferences on its bioavailability and potential ecological impact; (2) monitor Tl mass loads from these catchments and quantify the seasonal variability of pollutant discharge to the sea in different hydrological conditions, in view of the extreme weather events caused by climate change. This information is critical to assess the environmental impact on a biodiversity hotspot such as the Mediterranean Sea and to plan proper mitigation measures.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15070678/s1>, Table S1: Stream sediment data collected in 2022.

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Abbreviations

The following abbreviations are used in this manuscript:

MAMD	Monte Amiata Mining District
ASSM	Abbadia San Salvatore mine
ASRS	Abetina-Solforate-Rosselli-Schwarzenberg mines
FR	Fiora River
VcD	Vulci Dam
CSC	Italian concentration threshold for public soils of an element

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