Research article

Heavy metals in tributaries of Tiber River in the urban area of Rome (Italy)✩

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ARTICLE INFO

ABSTRACT

Both natural and anthropogenic activities are responsible for heavy metal abundance in the environment. Due to the high persistence, heavy metals can accumulate and remain in the sediment for very long periods, becoming a source of contaminants for aquatic biota. Within small urbanized watercourse catchments, the accumulation of heavy metals in bottom sediments takes place and sediments can be adopted as an efficient indicator for monitoring heavy metal pollution levels and pollution sources in aquatic environments.

Tiber River, the most polluted river among the 20 longest Italian rivers, has different tributaries distributed from north to south of Rome city. The aim of the study was to evaluate the heavy metal pollution in water and sediment of six Tiber River small tributaries through the use of land cover, water physico-chemical parameters and geochemical multi-index (Concentration factor, Pollution Load index, Enrichment factor and Geoaccumulation index).

The results indicate that in general the contamination of water and sediments is moderate as the threshold values are exceeded only by some metals and in some sites. As regards the indices that evaluate the enrichment factors, it has been seen that some sampling sites have high values of specific metal enrichment (As, Hg, Pb). A more compromised situation is highlighted by the Concentration Factor and the Pollution Load index where more than half of the sampling sites are found at levels of significant heavy metal pollution suggesting that point sources of heavy metals in the water and sediments should be closely monitored by the use of combined analysis.

1. Introduction

For years now, there has been an increasing ecological and global public health concern associated with environmental contamination by heavy metals due to their pervasiveness and persistence [1,2].

Both natural and anthropogenic activities are responsible for heavy metal abundance in the environment [3].

The increasing pollution by heavy metals has a significant adverse health effect for invertebrates, fishes, and humans [4–8]. They can disrupt the natural ecosystems both aquatic and terrestrial and impact the human body acutely and permanently through the food chain [9]. After release from both natural and anthropogenic sources, heavy metals contaminate natural water bodies, sediments, and soils. In the aquatic ecosystems the potentially toxic heavy metals are transported in dissolved or in particulate form. The primary

processes driving the interactions of heavy metals with water and sediments are: adsorption, desorption, dissolution and sedimentation. Suspended or settled metal particles as well as physical, chemical and biological parameters play an important role in these processes [10,11]. Due to the high persistence, heavy metals can accumulate and remain in the sediment for very long periods.

However, immobilized heavy metals do not necessarily stay in that condition, but may be released as a result of chemical changes in water or living organisms becoming a potential secondary pollution source [12].

Due to their possible introduction into the environment from widespread sources, heavy metals represent a group of pollutants of particular importance. At European level some heavy metals are included in different Directives that impose the concentration that should not be exceeded to protect human health and environment (Environmental Quality Standards, EQS). Moreover, some heavy metals are also included in the list of priority hazardous substances (2000/60/EC, 2008/105/EC and 2013/39/EU) [13–15].

In urban areas, rivers, as well as minor hydrographic network, have also been associated with water quality problems because of the practice of discharging of untreated domestic and industrial waste into the water bodies which leads to the increase in the level of metals in river water [16,17]. Within small urbanized watercourse catchments, the accumulation of heavy metals in bottom sediments takes place and sediments can be adopted as an efficient indicator for monitoring heavy metal pollution levels and pollution sources in aquatic environments [18]. In addition, due to the development of buildings and roads, the original environments, in particular the aquatic one, are increasingly reduced and the remaining ones are often associated with dangerous hygienic conditions. They are not an exception the small waterways in the urban and peri-urban areas for which a characterization is required to plan future interventions by restoration, in order to avoid a total and irreversible compromise and to conserve biodiversity.

In general, the results of many studies show that heavy metal concentrations can be ranked based on land use characteristics as follows: industrial region > urban region > agricultural region > natural fields [19].

Several researchers have attempted to evaluate heavy metal pollution levels of river sediments and investigate the correlation between heavy metals and land use to assist in land use and river pollution management planning. These previous studies reported that the higher the diversity of industrial and urban land or land use, the more negatively it affects sediment pollution [20–22].

Surface water are particularly vulnerable to changing in land use and ubiquitous exploitation. The deterioration of river ecosystems due to unsustainable human activities has become a key environmental concern. To identify primary threats to water quality is useful to understand the relationship between land use and water quality. These relationships are meaningful for effective water quality management because they can be used to target critical land use areas and to institute relevant measures to minimize pollutant loadings [23].

In Italy, the second biggest river and the most polluted among the 20 longest rivers of the Country is the Tiber River [24].

In the lower course of the Tiber River, after the confluence with the Aniene River, in the urban area of Rome (Italy) the water quality decreases dramatically due to discharges from intense industrial activities, several ditches, heavily urbanized watershed and agricultural waste [25,26].

Both Tiber and Aniene rivers, have different tributaries distributed from north to south of Rome city. This territory is characterized by a series of hilly complexes all derived from ancient volcanic systems. The dense network of watercourses, that crosses the territory, presents a siliceous substrate that characterizes both the chemistry and the biology of the ecosystems associated. Until the 70s, these small natural streams conveyed domestic and industrial waste waters directly into the Tiber River. The resulting chemical pollution and biological changes of streams and connected ground waters produced environmental degradation and hygienic problems [27–30]. To date, no scientific research regarding heavy metal pollution in water and sediment of the Tributaries of Tiber and Aniene has been conducted so far.

The aim of this study was to analyze the concentrations of 16 heavy metals, in water and sediments, of six tributaries in the urban and peri-urban area of Rome into the Tiber River basin. In addition, the study had the objective to evaluate the pollution level through
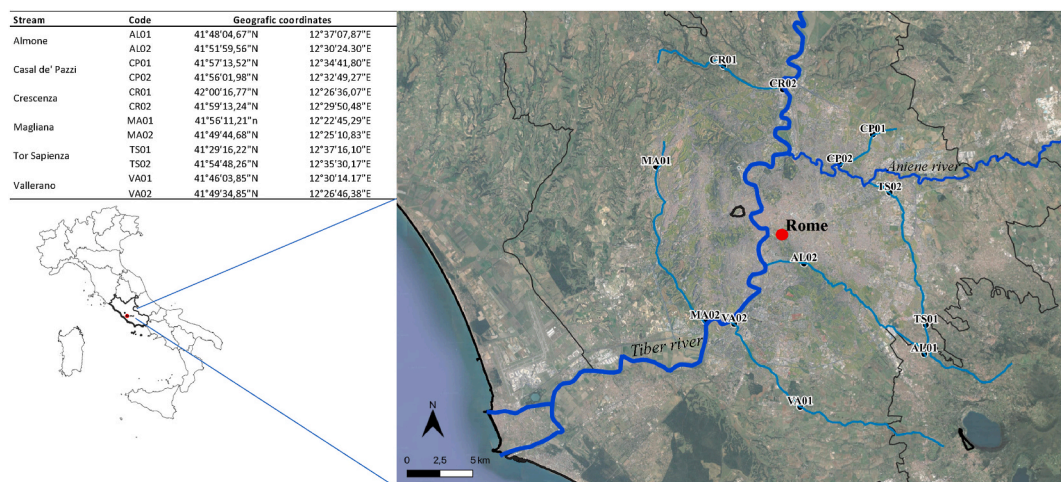

Fig. 1. Geolocalization and georeferentiation of Study area.

the use of multi-index geochemical analysis and to understand the relationship between heavy metal concentration and land use.

2. Material and methods

2.1. Study area

For each tributary we selected two sampling sites in order to compare the difference between the upstream (suburban) and the downstream (urban) point (Fig. 1). All the stream selected in this study belong to Italian hydroecoregion (HER) 14 *Roma-Viterbese.* This HER has a volcanic origin with siliceous substrate and tuff rocks.

2.2. Land cover data processing

We acquired thematic land cover classification maps from the Corine Land Cover 2018 (CLC), (https://land.copernicus.eu/pan-european/corine-land-cover). The Land cover analysis was performed using the QGIS software (version 3.28) selecting a buffer area of 1 km around our sampling sites. Intersecting the layer of CLC and the buffer area we calculate the Ha of the single CLC categories occurring in the buffer. From Ha, the total and the single sampling sites percentage of land cover classes were calculated.

2.3. Sampling and analysis

The study was conducted during the summer season (Low Flow) and included in field and in laboratory analysis. Physico-chemical parameters such as water temperature T ($^\circ$C), pH, electrical conductivity EC (mS/cm) and dissolved oxygen percentage of saturation (DO %) were measured in the field using a multiparameter probe (YSI).

One liter of raw water was collected using dark bottles previously rinsed with raw water for further chemical analysis. The nitrates NO_3^- (mg/L), orthophosphates PO_4^{3-} (mg/L), ammonium NH_4^+ (mg/L) and Chemical Oxygen Demand COD (mg/L) were determined according to protocols of SpectroQuant® (Merck) and five-day Biological Oxygen Demand BOD_5 (mg/L) were determined by measuring system OxiTop® WTW (VWR).

For heavy metal analysis we collected water and sediment samples as above described: for water, in each sampling site, three aliquots of 50 mL were collected in different point along bank-to-bank transect. The aliquots were mixed in order to obtain an integrated sample that was subsequently filtered with a 0.45 μm filters (cellulose nitrate, Millipore) into polypropylene tubes using a plastic syringe (50 mL). After acidification with HNO_3 (65 % supra pure, Merck), the samples were kept at 4 $^\circ$C in the dark until analysis.

Sediment samples were collected using a snapper sediment sampler with a plastic beaker attached. Three aliquots of 300 g each were collected in different point along bank-to-bank transect and transferred into a plastic bucket and mixed thoroughly to obtain an integrated sample. The sediment samples were transported into polythene bag to the laboratory where they were firstly air-dried at room temperature and then hand-sieved, through a 2 mm sieve, in order to remove the coarse material.

The determination of the concentration of heavy metals listed in Table 1 was performed by Regional Agency for Environmental Protection of Basilicata (ARPAB) laboratory using the EPA (Environment Protection Agency) method 3051A [31] followed by analysis using mass spectrometry (Mass Spectrometer Inductive Coupled Plasma (ICP-MS) model DRCE PerkinElmer).

Table 1
Heavy metal analyzed and their background values in lithosphere and soil [32].

Metal	Concentration (mg/kg)		
	Litosphere	Soil	Average
Al	82000.00	10000.00	46000.00
As	1.50	5.00	3.25
B	10.00	8.00	9.00
Be	2.60	3.00	2.80
Cd	0.18	1.00	0.59
Co	20.00	10.00	15.00
Cr tot	100.00	65.00	82.50
Cu	70.00	18.00	44.00
Fe	45000.00	50000.00	47500.00
Hg	0.05	0.03	0.04
Mn	950.00	950.00	950.00
Mo	1.50	0.50	1.00
Ni	75.00	20.00	47.50
Pb	14.00	32.00	23.00
V	160.00	90.00	125.00
Zn	80.00	100.00	90.00

2.4. Geochemical analysis

In the interpretation of geochemical data, choice of background values plays a significant contribution. Several researchers have used the lithosphere and soil abundance data as reference baselines (Table 1) [33–35]. The degree of contamination from heavy metals could be evaluated by determining the Contamination Factor (CF), Pollution Load Index (PLI), Enrichment Factor (EF) and Geo-Accumulation Index (I_{geo}) [36].

2.5. Contamination factor (CF) and pollution load index (PLI)

The ratio of the measured concentration to natural abundance of a given metal had been proposed as the contamination factor (CF) being classified into four grades (CF < 1 low contamination, 1 < CF < 3 moderate contamination, 3 < CF < 6 considerable contamination and CF > 6 very high contamination) for monitoring the pollution of one single metal over a period of time [37]: CF_{metals} is the ratio between the content of each metal to the background values (background value from the average shale value) in sediment:

$$CF_{metals} = C_{metal}/C_{background} \tag{1}$$

To evaluate the sediment quality, combined approaches of pollution load index were calculated according to Islam et al. [37]. The PLI is defined as the nth root of the multiplications of the contamination factor of metals (CF).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n} \tag{2}$$

Therefore, PLI value of zero indicates excellence, a value of one indicates the presence of only baseline level of pollutants and values above one indicates progressive deterioration of the site and estuarine quality [38]. The PLI gave an evaluation of the overall toxicity status of the sample and also it is a consequence of the contribution of the studied metals.

2.6. Enrichment factor (EF) and geoaccumulation index (Igeo)

Enrichment factor (EF) is considered as an effective tool to evaluate the magnitude of contaminants in the environment [39], classifying the soil dust quality in five classes (Table 2). Several methods of normalization are possible, ranging from the use of simple metal normalization ratios to more complex methods based on regression analysis [40]. In this paper we normalized metal concentrations as ratios to iron as another constituent of the soil. The EF for each element was calculated to evaluate anthropogenic influences on heavy metals in sediments using the following formula [41]:

$$EF = (Metal/Fe)Soil \, / \, (Metal/Fe)Background \tag{3}$$

Where (Metal/Fe)Soil is the ratio of concentration of heavy metal to that of Iron in the sediment sample, and (Metal/Fe)Background is the same reference ratio in the background sample.

The Igeo gives similar information as EF. The geoaccumulation index (Igeo) was defined by Muller [42] for metal concentrations in the 2-μm fraction and was developed for global standard shale values. This index is expressed as follows:

$$Igeo = \log_2 /[Cn/(1.5^* \, Bn)] \tag{4}$$

Where Cn is the measured concentration in the sediment for the n-esim metal, Bn is the background value for the n-esim metal and the factor 1.5 is used because of the possible variations in the background data due to the lithological changes.

The background values of the metals of interest used to calculate Igeo were the same as those used in the aforementioned EF calculations. Muller [43] has defined seven classes of the geoaccumulation index (Table 3).

2.7. Statistical analysis

Physico-chemical and heavy metal in water and sediment data were statistically analyzed using Agglomerative Hierarchical Clustering (AHC) based on the Bray-Curtis dissimilarity index [44]. The Principal Component Analysis (PCA), using Pearson correlation coefficient as similarity index [45] was performed for the ordination of sampling stations using heavy metals (sediment and water) and land cover data as parameters (PAST version 4.03).

Table 2
Value and relative soil dust quality of enrichment factor [39].

Value	Soil dust quality
EF < 2	Deficiency to minimal enrichment
2< EF < 5	Moderate enrichment
5< EF < 20	Significant enrichment
20< EF < 40	Very high enrichment
EF > 40	Extremely high enrichment

Table 3
Classes and relative value of soil dust quality in I_{geo} index [42].

Class	Value	Soil dust quality
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderatelly contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated
4	$3 < I_{geo} < 4$	Heavily contaminated
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated
6	$I_{geo} \geq 5$	Extremely contaminated

3. Results and discussion

3.1. Land cover

The analysis of the land cover performed on the area of all the sampling stations showed that *Discontinuous urban fabric* and *Non-irrigated arable land* are the most present categories with approximately 28 % of coverage each. These are followed by *Complex cultivation patterns* and *Land principally occupied by agriculture, with significant areas of natural vegetation* (Fig. 2).

The results of land cover analysis, performed on each water body, are shown in Fig. 3. The percentages of urban area compared to those for agricultural use are higher in the downstream sites with the exception of some sampling sites included in urban parks (i.e. AL02 in the Appia Antica park and CP02 in Valle dell' Aniene park). The presence of urban green areas represents an important contribution to the reduction of heavy metals in water and sediments. In watercourses aquatic plants (macrophytes) are able to absorb and accumulate heavy metals [46].

It should be also underlined that some sites are characterized by a significant percentage of *industrial or commercial units* that can provide a different contribution to heavy metal pollution (CP01, CR02, TS02).

3.2. Physico-chemical analysis

The physico-chemical parameters have a non-homogeneous pattern both for watercourse and sampling site, showing as, from upstream to downstream, the different anthropic pressures exerted on diches can influence their physico-chemical features.

In particular, in two sites, CP02 and TS02, dissolved O_2 was very low. Whereas high levels of nitrates were found in 6 of the 12 sampling sites. High conductivity values have been observed in both sampling sites of Crescenza stream and in TS02. In approximately half of sampling stations both Chemical and Biological oxygen demand (COD and BOD_5) had high level showing a significant presence of organic pollutant (supplemental material SM1). It is well known that physico-chemical parameters show seasonal variation [47]. In this study, performed in a one-sampling campaign this analysis has been used as support to evaluate possible critical issues in single sampling stations. In addition, the results of physico-chemical analysis were used in statistical analysis in order to evaluate the similarity among the different sampling stations.
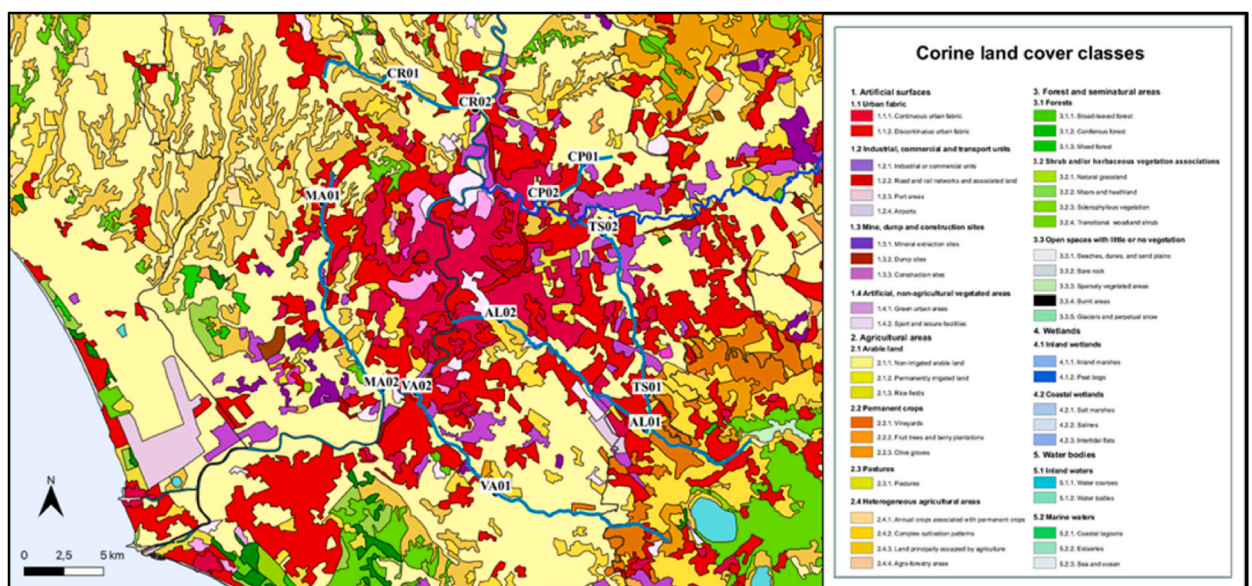

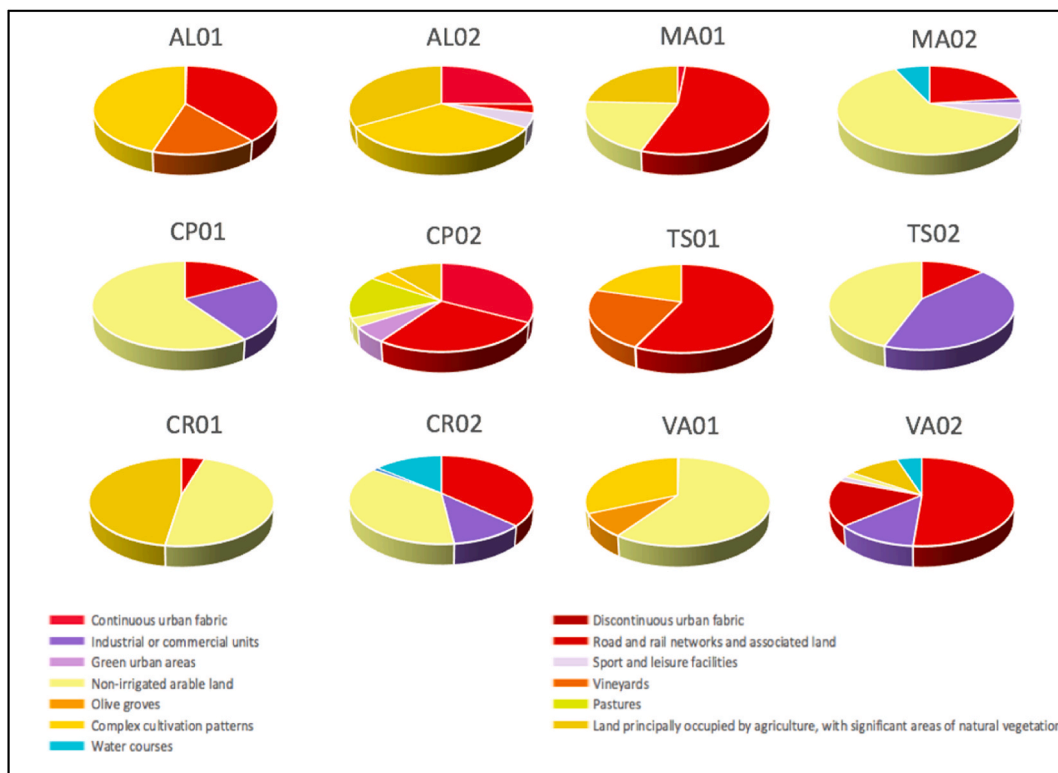**Fig. 2.** Land cover in the study area of 6 small watercourses.

Fig. 3. Percentage of land cover classes in sampling stations of the six different tributaries of this study.

3.3. Heavy metal analysis

Concerning the concentration of heavy metals in sediments and surface water, the current European and Italian regulations do not assess limit values. For these reason in this paper, we have considered the values defined by the decree 152/2006 [48] relative to public, private and residential green area for sediments whereas the values relative to groundwater for surface water.

Not all the heavy metals considered in this study exceeded the limit values defined by Decree 152/2006. For some heavy metals such as Mn, the value limit in soil is not defined. For other, i.e. Ni, the values were significantly lower than those defined by the decree.

Heavy metal concentrations in sediment and surface water are reported in SM 2 and 3.

In Fig. 4 we report the metal concentrations in sediments which in the different stations resulted higher than the limit values. B, Co and Zn exceeded the limits in all stations. Al01 showed values above the limits for all metals, a similar result was observed in CP02 station except for Cu which remained under the limit. These results could be due to both natural contribution (Volcanic sediments) and diffuse pollution in the areas surrounding the watercourses [49,50].

In water samples, the number of heavy metals with concentration exceeding the limits is reduced compared with sediments (Fig. 5). Berillium exceeded the limit value in all stations, and was particularly high in CR02 and CR01 stations where high concentration of As were also observed. In MA01 and VA01 elevated values of Mn were found. It is important to outline that many sampling stations are characterized by a clay component able to adsorb the metals limiting their dissolution in water [51].

Overall, the results indicate that heavy metal contamination of water and sediments is moderate as the thresholds are exceeded only by some metals and in some sampling sites. Some studies focused on temporal and seasonal distribution of heavy metal in order to evaluate the effects of surface runoff, temperature and river flow on heavy metal distribution [52,53]. The present study cannot provide information on seasonal variation of heavy metal contamination, it was conducted in a single sampling campaign, during the summer season and had the objective to propose a methodological approach to evaluate the heavy metal contamination.

3.4. Contamination factor (CF) and pollution load index (PLI)

A very high enrichment was found for As with CF values higher than 3 in almost all stations. High values of CF were found also for Cu in AL02, for Hg in AL02, CP01, CP02 and CR02. Pb shows high CF in AL02, CP01, CP02, CR02, MA01 and VA01.

None of the stations showed an excellent status (PLI = 0), only baseline level of pollution was found in AL01, CR01, MA02, TS01, TS02, VA01, VA02 (PLI between 0 and 1). A progressive deterioration was found in AL02, CP01, CP02, CR02, MA01 which showed a PLI above 1 (Table 4).

A similar situation was found when referred to soil. Extremely or very high enrichment was found for Hg in AL02 and CP02,
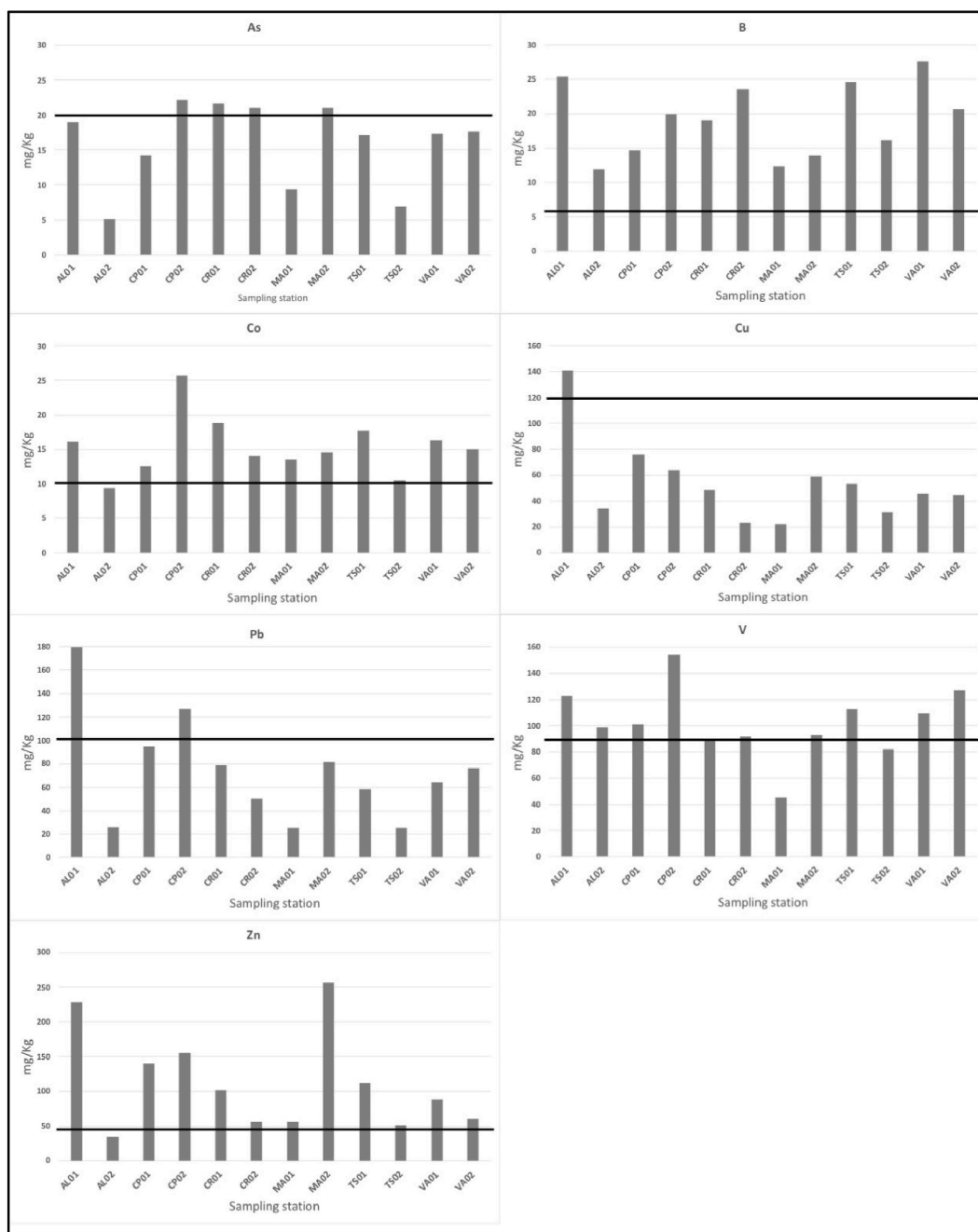
Fig. 4. Metals in sediments with a threshold value higher than the limits indicated in the Legislative Decree 152/2006.

respectively. Minimal enrichment was noted for Cd, Cr tot, Fe, Mn, Mo, in all stations. From moderate to significant enrichment was found for the remaining metals depending from the different stations (Table 6).

3.5. Geoaccumulation index (Igeo)

I$_{geo}$ results revealed that almost all the sites in the study area were not or moderately contaminated with respect to almost all heavy metals both using lithosphere and soil average (Tables 7 and 8). AL01, CP01, CR01, CR02, MA01, TS01, VA01 and VA02 resulted from moderately to heavily contaminated for As in using lithosphere average. CP02 station resulted heavily/extremely contaminated by Hg both using lithosphere and soil average.

The different results between the EF and I$_{geo}$ indices was probably due to the use of Al as the reference element in the EF calculation.
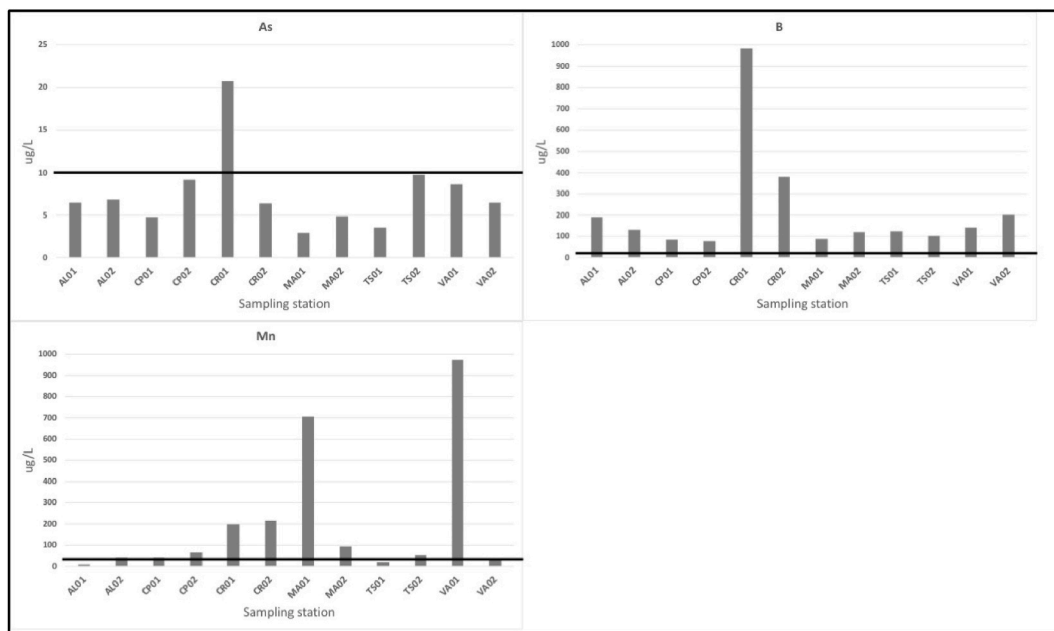
Fig. 5. Metals in water with a threshold value higher than the limits indicated in the Legislative Decree 152/2006.

Table 4
Concentration Factor and Pollution Load index results.

Metal	Sampling station											
	AL01	AL02	CP01	CP02	CR01	CR02	MA01	MA02	TS01	TS02	VA01	VA02
Al	0.52	1.16	1.20	0.60	0.80	1.00	0.93	0.38	0.63	1.02	1.18	1.18
As	1.57	5.86	6.84	4.37	6.46	6.68	6.49	2.89	2.13	5.27	5.43	5.32
B	1.33	2.82	2.21	1.64	2.61	2.12	1.55	1.37	1.80	2.74	2.30	3.07
Be	0.81	2.59	3.08	1.39	1.93	2.41	2.17	0.63	1.04	1.91	2.19	1.98
Cd	0.17	1.98	0.26	0.26	0.17	0.29	0.59	0.19	0.17	0.20	0.17	0.17
Co	0.63	1.08	1.72	0.84	0.94	1.26	0.97	0.90	0.70	1.18	1.00	1.09
Cr tot	0.08	0.33	0.28	0.23	0.14	0.43	0.26	0.41	0.08	0.17	0.19	0.13
Cu	0.78	3.21	1.46	1.72	0.53	1.10	1.34	0.50	0.71	1.21	1.01	1.04
Fe	0.42	0.66	1.04	0.57	0.56	0.75	0.66	0.46	0.41	0.60	0.61	0.54
Hg	2.50	11.47	3.26	80.09	2.50	6.97	2.50	2.50	2.50	2.50	2.50	2.50
Mn	0.41	0.52	1.06	0.40	0.98	0.97	0.71	0.77	0.37	0.52	0.67	0.59
Mo	0.10	0.26	0.23	0.43	0.39	0.36	0.43	0.20	0.13	0.37	0.17	0.24
Ni	0.41	0.61	0.57	0.53	0.32	0.76	0.60	0.77	0.45	0.50	0.41	0.36
Pb	1.14	7.82	5.52	4.13	2.19	3.42	3.55	1.10	1.10	2.56	3.33	2.79
V	0.79	0.98	1.23	0.81	0.73	0.71	0.74	0.36	0.66	0.90	1.02	0.88
Zn	0.39	2.53	1.73	1.56	0.63	1.12	2.85	0.63	0.56	1.25	0.68	0.98
PLI	**0.57**	**1.49**	**1.25**	**1.14**	**0.85**	**1.19**	**1.13**	**0.69**	**0.62**	**0.97**	**0.91**	**0.90**

Enrichment factor (EF) Fe normalized.

When referred to lithosphere average values, clear signs of enrichment was present for Hg in station CP02. Very high or significant enrichment is present in all station for As. Moderate or significant enrichment was noted for Pb in almost all stations. Minimal enrichment was noted for Co, Cr$_{tot}$, Fe, Mn, Mo, Ni and V in all stations (Table 5).

The concentration of heavy metal in lithosphere and soil could be different by location [54] and could result in an overestimation or underestimation of the enrichment factor [55].

Overall, the results of a multi-index analysis agree with other studies on the pollution by specific heavy metal especially in urban areas. Yang et al. [56] report that the high Pb, Zn, Cu, Cd, and Hg pollution levels were closely related to domestic sewage and industrial wastewater. Another study relates source of Cd, Cu, Pb and Zn in urban soils with anthropogenic sources and Cr and Ni mainly from natural sources [57].

According to the literature the atmospheric deposition, vehicular activities, and metallic building envelopes are the major pollution sources in the urban environment and have been studied far more extensively than other sources [58].

Due to vehicle traffic and land use, Pb pollution from anthropic source was high in urban area. High level of Zn, Cu, and Cd contamination could come from vehicles tire wear, brake pads and lubricants, household waste, and construction activities. Industrial

Table 5
Enrichment factor using lithosphere average as background values.

Metal	Sampling station											
	AL01	AL02	CP01	CP02	CR01	CR02	MA01	MA02	TS01	TS02	VA01	VA02
Al	0.66	0.94	0.61	0.56	0.75	0.70	0.74	0.45	0.83	0.90	1.03	1.17
As	7.71	18.33	13.55	15.62	23.49	18.18	20.05	12.96	10.71	17.94	18.28	20.38
B	2.72	3.66	1.82	2.43	3.94	2.39	1.99	2.56	3.77	3.87	3.21	4.89
Be	1.99	4.03	3.04	2.47	3.48	3.27	3.34	1.40	2.60	3.22	3.67	3.78
Cd	1.26	9.39	0.78	1.39	0.93	1.20	2.76	1.26	1.29	1.03	0.86	0.98
Co	1.06	1.17	1.18	1.04	1.18	1.18	1.04	1.40	1.23	1.39	1.17	1.45
Cr tot	0.15	0.39	0.21	0.31	0.19	0.45	0.31	0.70	0.16	0.22	0.24	0.20
Cu	1.11	2.91	0.84	1.79	0.56	0.87	1.20	0.65	1.04	1.20	0.99	1.16
Hg	4.54	13.24	2.38	105.69	3.35	7.00	2.85	4.14	4.64	3.14	3.11	3.54
Mn	0.94	0.75	0.97	0.66	1.65	1.21	1.01	1.60	0.85	0.81	1.05	1.05
Mo	0.15	0.25	0.14	0.47	0.43	0.30	0.41	0.28	0.20	0.38	0.18	0.29
Ni	0.59	0.56	0.33	0.56	0.34	0.61	0.54	1.01	0.67	0.50	0.41	0.40
Pb	4.25	18.53	8.29	11.20	6.03	7.06	8.33	3.73	4.21	6.60	8.50	8.11
V	1.40	1.11	0.88	1.04	0.96	0.70	0.83	0.59	1.19	1.11	1.23	1.21
Zn	1.00	4.11	1.78	2.89	1.19	1.59	4.58	1.46	1.47	2.21	1.19	1.96

Table 6
Enrichment factor using soil average as background values.

Metal	Sampling station											
	AL01	AL02	CP01	CP02	CR01	CR02	MA01	MA02	TS01	TS02	VA01	VA02
Al	6.05	8.59	5.60	5.07	6.87	6.42	6.78	4.06	7.53	8.18	9.37	10.67
As	2.57	6.11	4.52	5.21	7.83	6.06	6.68	4.32	3.57	5.98	6.09	6.79
B	3.77	5.09	2.53	3.38	5.47	3.32	2.77	3.56	5.24	5.37	4.46	6.79
Be	1.92	3.88	2.93	2.38	3.35	3.14	3.21	1.35	2.51	3.10	3.54	3.64
Cd	0.25	1.88	0.16	0.28	0.19	0.24	0.55	0.25	0.26	0.21	0.17	0.20
Co	2.37	2.59	2.62	2.30	2.62	2.63	2.32	3.11	2.72	3.09	2.59	3.21
Cr tot	0.25	0.67	0.37	0.53	0.33	0.77	0.52	1.20	0.27	0.37	0.41	0.33
Cu	4.81	12.57	3.62	7.71	2.40	3.75	5.18	2.79	4.50	5.17	4.26	5.00
Hg	8.40	24.53	4.41	195.73	6.21	12.96	5.28	7.67	8.60	5.82	5.76	6.55
Mn	1.04	0.84	1.08	0.73	1.83	1.35	1.13	1.77	0.94	0.90	1.16	1.17
Mo	0.50	0.83	0.47	1.57	1.45	1.01	1.36	0.93	0.68	1.28	0.60	0.96
Ni	2.46	2.34	1.37	2.31	1.43	2.53	2.25	4.20	2.78	2.08	1.70	1.68
Pb	2.07	9.01	4.03	5.45	2.93	3.43	4.05	1.81	2.05	3.21	4.13	3.94
V	2.77	2.19	1.74	2.06	1.90	1.38	1.64	1.16	2.35	2.19	2.44	2.40
Zn	0.89	3.65	1.58	2.57	1.05	1.41	4.07	1.30	1.31	1.96	1.06	1.74

Table 7
I_{geo} using lithosphere average as background values.

Metal	Sampling station											
	AL01	AL02	CP01	CP02	CR01	CR02	MA01	MA02	TS01	TS02	VA01	VA02
Al	−1.63	−0.83	−0.80	−1.49	−1.20	−0.98	−1.06	−1.94	−1.44	−0.96	−0.82	−0.82
As	0.82	2.14	2.29	1.84	2.23	2.27	2.24	1.43	1.12	2.03	2.06	2.04
B	−0.23	0.53	0.28	−0.02	0.45	0.24	−0.07	−0.19	0.08	0.50	0.32	0.61
Be	−0.54	0.62	0.80	0.00	0.32	0.55	0.44	−0.80	−0.29	0.31	0.45	0.35
Cd	−0.99	1.47	−0.57	−0.58	−0.99	−0.45	0.26	−0.90	−0.99	−0.82	−0.99	−0.99
Co	−1.16	−0.62	−0.15	−0.87	−0.76	−0.47	−0.72	−0.80	−1.04	−0.53	−0.69	−0.61
Cr tot	−3.13	−1.71	−1.86	−2.07	−2.58	−1.44	−1.94	−1.48	−3.08	−2.39	−2.26	−2.61
Cu	−1.12	0.30	−0.49	−0.33	−1.51	−0.77	−0.58	−1.57	−1.21	−0.68	−0.86	−0.83
Fe	−1.22	−0.77	−0.32	−0.91	−0.92	−0.63	−0.76	−1.13	−1.25	−0.86	−0.85	−0.98
Hg	0.29	1.81	0.55	3.75	0.29	1.31	0.29	0.29	0.29	0.29	0.29	0.29
Mn	−1.29	−1.05	−0.34	−1.32	−0.42	−0.44	−0.75	−0.67	−1.41	−1.07	−0.80	−0.93
Mo	−3.11	−2.17	−2.28	−1.66	−1.76	−1.82	−1.66	−2.41	−2.84	−1.81	−2.56	−2.22
Ni	−1.75	−1.35	−1.43	−1.49	−1.99	−1.13	−1.38	−1.13	−1.65	−1.55	−1.74	−1.89
Pb	0.22	2.15	1.80	1.51	0.87	1.32	1.36	0.18	0.19	1.03	1.29	1.12
V	−0.89	−0.67	−0.44	−0.87	−0.96	−0.99	−0.95	−1.67	−1.07	−0.75	−0.64	−0.78
Zn	−1.22	0.64	0.26	0.15	−0.75	−0.17	0.76	−0.75	−0.86	−0.06	−0.67	−0.30

Table 8

I$_{geo}$ using soil average as background values.

Metal	Sampling station											
	AL01	AL02	CP01	CP02	CR01	CR02	MA01	MA02	TS01	TS02	VA01	VA02
Al	0.47	1.27	1.30	0.61	0.90	1.12	1.05	0.16	0.67	1.14	1.29	1.29
As	−0.39	0.93	1.09	0.64	1.03	1.06	1.03	0.22	−0.08	0.83	0.86	0.83
B	0.00	0.75	0.51	0.21	0.67	0.46	0.15	0.03	0.30	0.72	0.54	0.83
Be	−0.68	0.48	0.65	−0.15	0.18	0.41	0.30	−0.94	−0.43	0.17	0.31	0.21
Cd	−2.71	−0.25	−2.28	−2.29	−2.71	−2.16	−1.46	−2.61	−2.71	−2.54	−2.71	−2.71
Co	−0.47	0.07	0.54	−0.18	−0.06	0.23	−0.03	−0.10	−0.35	0.17	0.00	0.09
Cr tot	−2.70	−1.28	−1.43	−1.64	−2.15	−1.01	−1.51	−1.05	−2.65	−1.96	−1.83	−2.18
Cu	0.24	1.65	0.86	1.03	−0.15	0.58	0.78	−0.21	0.15	0.68	0.50	0.53
Fe	−1.33	−0.88	−0.42	−1.01	−1.03	−0.74	−0.87	−1.24	−1.35	−0.96	−0.95	−1.08
Hg	0.80	2.32	1.06	4.27	0.80	1.82	0.80	0.80	0.80	0.80	0.80	0.80
Mn	−1.29	−1.05	−0.34	−1.32	−0.42	−0.44	−0.75	−0.67	−1.41	−1.07	−0.80	−0.93
Mo	−2.01	−1.07	−1.19	−0.56	−0.66	−0.73	−0.56	−1.31	−1.74	−0.71	−1.46	−1.12
Ni	−0.43	−0.03	−0.11	−0.17	−0.67	0.19	−0.05	0.20	−0.33	−0.23	−0.42	−0.56
Pb	−0.60	1.32	0.97	0.68	0.05	0.49	0.53	−0.64	−0.64	0.20	0.47	0.29
V	−0.31	−0.09	0.13	−0.29	−0.39	−0.42	−0.37	−1.09	−0.50	−0.18	−0.06	−0.21
Zn	−1.44	0.42	0.04	−0.07	−0.98	−0.39	0.54	−0.98	−1.08	−0.29	−0.90	−0.53

and transportation dust has also been reported as a major source of Hg [59]. Arsenic has high concentrations in volcanic-sedimentary aquifer in central Italy, but it is also known to be introduced into aquatic environments by the use of pesticides (insecticides and herbicides) in agriculture [60,61].

3.6. Statistical analysis

Bray- Curtis similarity index shows how all stations have a similarity equal to or greater than 75 % (Fig. 6). The cluster analysis divides sampling stations into two big groups but the greater similarity of the stations does not follow an order by stream or by location (upstream or downstream). This is probably due to the contributions of heavy metals and chemical-physical characteristics of watercourses depending on land cover in the surrounding area which can change regardless of their geographical location.

The PCA biplot in Fig. 7 expresses the relationship between heavy metals, land use, and sites among the sediment samples of the six tributaries selected in this study. The two extracted factors (PC1 and PC2) had a cumulative variance of 60,5 %. The first factor (PC1: 42,1 % of variance) was confirmed as a variable contributing to CLC classes *Industrial, commercial and transport units* and *inland waters*; the second factor (PC2: 18,4 % of variance) was confirmed as a variable contributing to CLC classes *Urban fabric*, *Artificial non-agricultural vegetated areas* and *Pastures* for the Almone stations and TS01 and CP02.
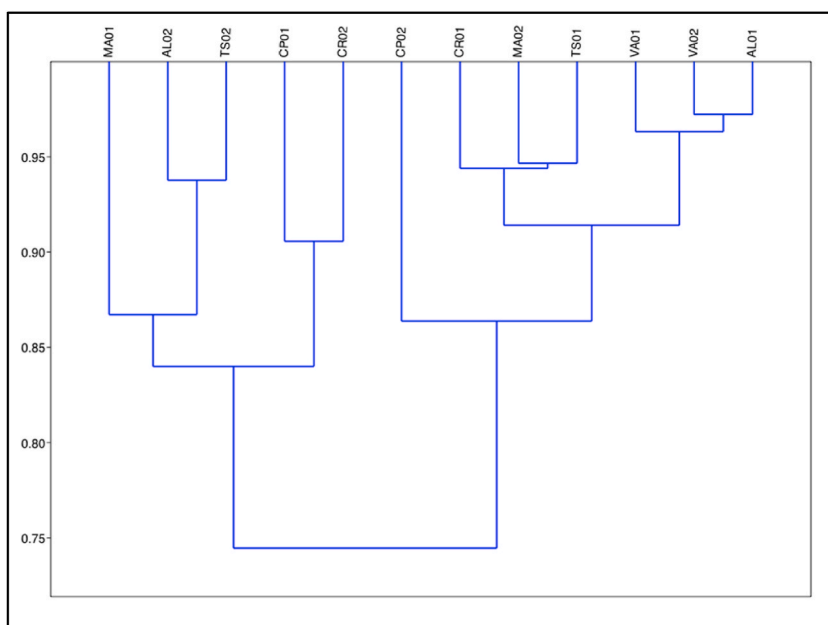

Fig. 6. Dendrogram produced by cluster analysis based on Bray- Curtis similarity index using value of heavy metals in water and sediment and physico-chemical parameters.
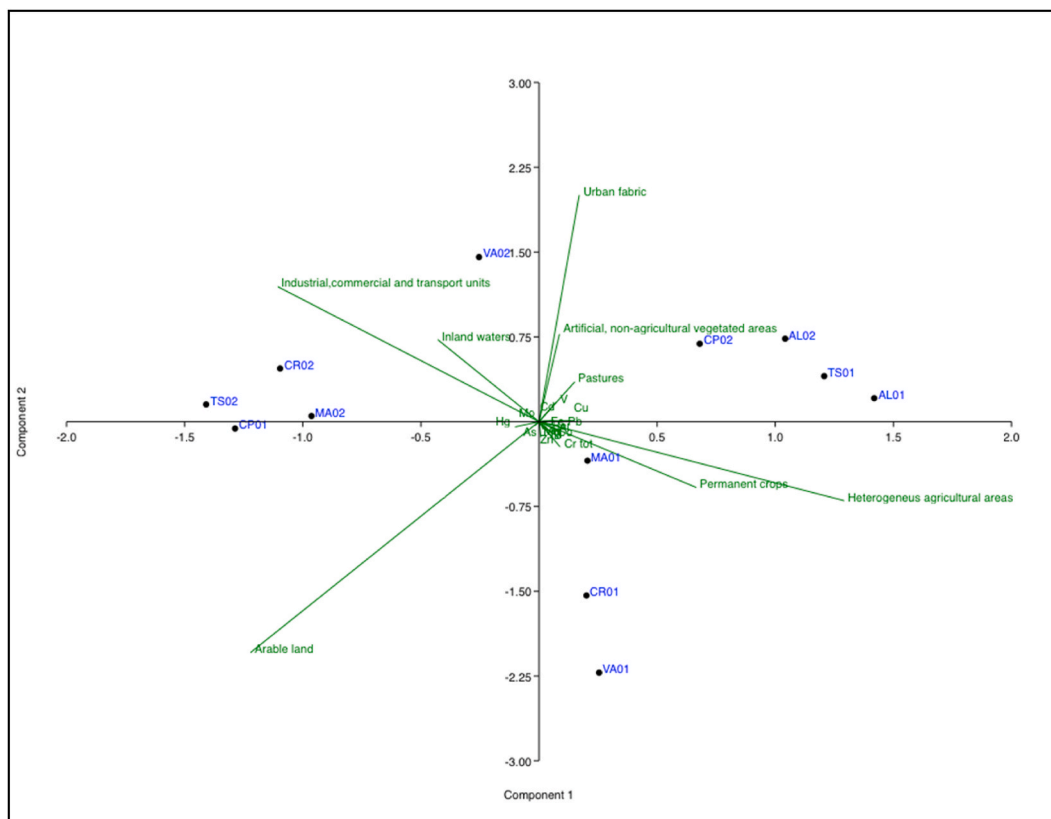
Fig. 7. Relationship between land use and heavy metals in sediment. Principal component analysis (PCA) biplot. PC1-principal component 1, PC2-principal component 2.

The PCA biplot in Fig. 8 expresses the relationship between heavy metals, land use, and sites among the water samples of the six tributaries selected in this study. The two extracted factors (PC1 and PC2) had a cumulative variance of 61,6 %. The first factor (PC1: 38,3 % of variance) was confirmed as a variable contributing to Al, Mo and to CLC classes *Heterogenous agricultural areas* and *Permanent crops*; the second factor (PC2: 23,3 % of variance) was confirmed as a variable contributing to Mn, Fe and CLC class *Arable land*.

4. Conclusions

Surface waters have natural sediments and nutrients deposited in them from the earth by natural processes. However, as internal uses and land cover change due to human development, can provide excessive levels of nutrients and contaminants.

Tiber River basin accounts as one of the main contribution sources of heavy metals in the Mediterranean Sea. Different tributaries in the urban and peri-urban area of Rome conveyed domestic and industrial waste water directly into the Tiber River contributing to the heavy metal pollution and creating an adverse effect on this riverine ecosystem. In the present study heavy metal pollutants were analyzed in six tributaries of Tiber and Aniene rivers.

A multi-index geochemical analysis indicated elevated heavy metal concentrations in all sediments analyzed in the selected river ecosystems.

In particular:

- The Contamination Factor (CF) highlights low or moderate contamination for most of metals and sampling stations, except for a compromised situation for As, Hg and Pb at almost all sampling sites.
- The Pollution Load index (PLI) showed that sediment samples have a baseline level of pollution in 7 sampling sites and a moderate pollution in 5 sites. The lowest PLI value were found mostly in the upstream sampling sites.
- The Enrichment Factor (EF) revealed that sampling sites are moderate or extremely enriched for As, Hg and Pb
- The Geoaccumulation index (I_{geo}) revealed that no contamination or moderately contamination occur in sampling sites

Although some limitations are present, such as the short time span and the small sample size, the results of the study show that the use of an integrated analysis, including physico-chemical parameters, geochemical indices and land cover, can provide a useful guidance for the prevention and management of heavy metal pollution in urban and peri-urban rivers such as in Rome.
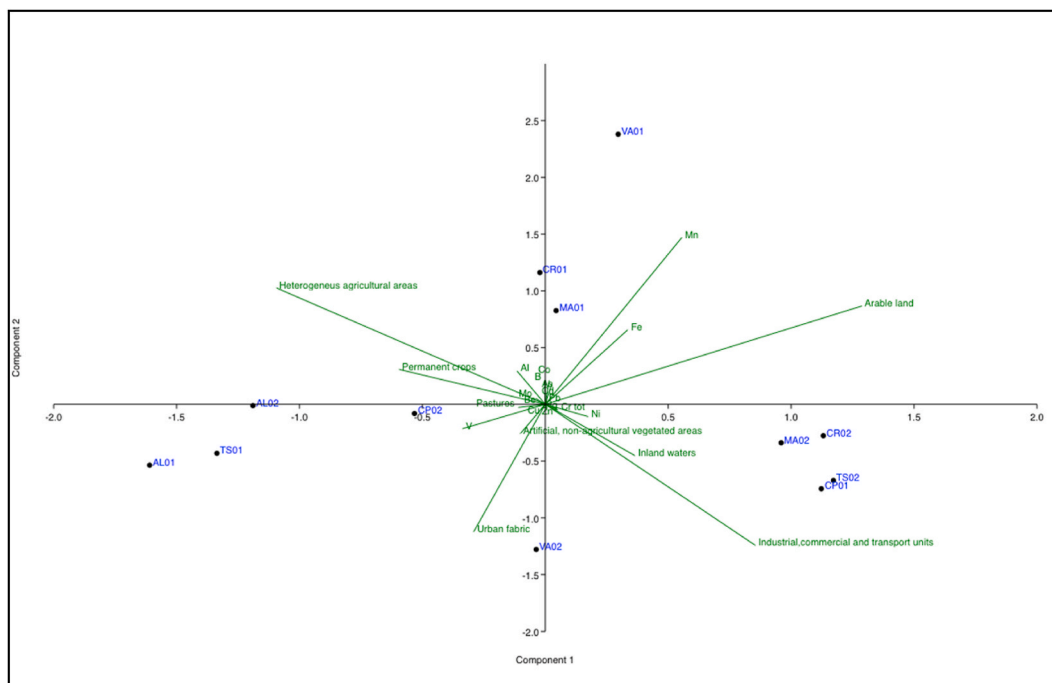
Fig. 8. Relationship between land use and heavy metals in water. Principal component analysis (PCA) biplot. PC1-principal component 1, PC2-principal component 2.

CRediT authorship contribution statement

F. Chiudioni: Writing – original draft, Formal analysis, Conceptualization. **S. Marcheggiani:** Writing – original draft, Supervision, Methodology. **C. Puccinelli:** Writing – review & editing, Formal analysis. **T. Trabace:** Writing – review & editing, Investigation. **L. Mancini:** Writing – review & editing, Supervision, Funding acquisition.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e33964.

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