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Concentrations of Potentially Toxic Elements in Topsoils of Urban Agricultural Areas of Rome

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Abstract: Urban agricultural soils have important social, environmental, and economic roles in big cities, contributing to their sustainability. However, food production in urban soils may be compromised due to soil pollution that resulted from decades of industrial, non-regulated environmental activity and mobile transport. In this study, 12 soils from the urban agricultural area of Rome (Italy) were analyzed for the potentially toxic elements (PTEs) Be, Ba, Pb, Co, Ni, V, Zn, Hg, Cd, As, Cu, and Cr. All but one of the soils under analysis were characterized by at least one PTE concentration above the threshold limit defined by the D.Lgs 152/06 for agricultural soils. Multivariate analysis showed that the soils could be classified into five clusters: clusters I and II had relatively lower mean PTE concentrations; clusters III, IV, and V had relatively higher mean PTE concentrations with several PTE concentrations above the threshold proposed by ILD. Three factors contributing to the variability of the PTE's concentration in the soils under investigation were identified: a geological factor related to PTE As, Ba, Be, and V; an anthropogenic factor related to Pb and Cu; and a mixed factor related to Co, Cr, Ni, and Zn. High PTE content may limit the utilization of urban soils for food production.

Keywords: Rome soils; urban soils; potentially toxic elements; metal ions; soil pollution; multivariate analysis

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1. Introduction

Urban soil pollution is a multifaceted and dynamic challenge, marked by the intricate interplay of various pollution sources and their far-reaching impacts on soil properties. The distinction between point and diffuse sources of pollution underscores the complexity, with diffuse pollution posing significant threats to the biochemical and microbiological aspects of soil [1–5]. The severity of pollution from metals and potentially toxic elements (PTEs) in urban soils is evident, with key contributors including the metallurgical industry, mining activities, fossil fuel consumption, vehicular traffic, irrigation, waste incineration, and fertilizer/agrochemical use [5–10]. The concentration and intensity of emission sources in urban areas lead to the redistribution of pollutants over significant distances [5,11–13].

In response to this intricate issue, Serrani et al. [5] proposed a "threshold of attention" for metals, providing a practical limit adaptable to evolving pollution sources and remediation efforts. Various anthropogenic activities contribute to the presence of these PTEs in urban environments, including industrial processes, soil pollution, landfills, tailings ponds, and the use of agricultural fertilizers and pesticides [14–16]. Italy, in addressing environmental concerns, has implemented the Directive through Legislative Decree 152/2006, known as the "Single Environmental Text", consolidating environmental laws into a unified legislative text (European Union Report: Status of Implementation of EU Environmental Laws in Italy, IP/A/ENVI/IC/2006-183, November 2006) [17].

Despite a global lack of comprehensive data on metal contamination, Tóth et al. [18] conducted a detailed analysis of metal content in agricultural topsoils across the European Union. With a growing urban population, the entry of PTEs into human bodies via multiple exposure pathways becomes a critical concern, emphasizing the need for precise risk characterization in health assessments [19,20]. Urban areas cover about 6% of Europe's total area, with 52% of the global population residing in urban or peri-urban regions [21–23]. The dynamic nature of urban environments, influenced by construction, use, and renewal processes, highlights the significant impact on urban landscapes [23,24]. The complexity of urban soils, influenced by various factors like construction remnants and drainage processes, challenges conventional assessment methods [22,25]. Agricultural practices, including prolonged flooding, terracing, and deep plowing, also impact soils, with altered soils resulting from human-induced changes exhibiting mixing and the presence of anthropogenic horizons [23,25].

The presence of pollutants, especially PTEs, in landfill leachate poses a serious threat to public health and ecosystems [26–28]. Soil, as the ultimate sink for metals, accumulates these pollutants via interactions with inorganic and organic matter [28]. Heavy metals (Cd, Ba, Hg, and Pb) have the potential to enter the food chain, posing health risks via consumption, dermal contact, ingestion, and inhalation [28–30], whereas toxic metals (Cr, Mn, Cu, and As) pose health risks via drinking water and the inhalation of soil particles [28,31,32].

In Europe, PTE contamination is a significant concern, with an estimated 2.5 million potentially contaminated sites [33]. The LUCAS Topsoil Survey provides a detailed overview of PTE concentrations in the topsoil of the European Union, supporting local assessments and potential control measures [34,35]. A comprehensive study on Palermo's urban soils investigated mineralogy, geochemistry, and concentrations of 11 heavy metals, offering insights into metal sources and contamination [36–38]. Peri-urban agriculture, situated between urban and rural zones, plays a pivotal role in global urban development [39,40]. However, PTE contamination in peri-urban agricultural soils poses health risks for adults and children in vegetable production, as revealed by a recent meta-analysis [41]. The challenges of soil pollution in urban areas, driven by industrialization, urbanization, and transportation, necessitate quick and simple methods for assessing urban soil quality [42–46]. The recognition of Technosols as Soil of the Year 2020, characterized by strong human influence, adds significance to understanding urban soil dynamics [47]. Inorganic contaminants in urban soils, including heavy metals like Pb, Zn, Cr, Ni, or Cd, resist decomposition by microorganisms, posing long-term toxicity to plants, animals, and humans [48–51].

Recent data from the Rapid Alert System for Food and Feed (RASFF) database highlight Italy's position as the "topmost notifying country" for heavy metals in food and feed, particularly for cadmium, mercury, chromium, and nickel, whereas in the RASFF notifications for Pb, Italy was ranked the second most commonly involved "country of origin" [52]. A chapter on soil governance in the European Union critiques existing strategies and advocates for a unified EU soil protection framework [53]. Using the fractal/multifractal method, a study mapped potentially toxic element distribution in Salerno, offering insights for enhanced environmental management [54]. The spatial diversity of urban soils is heightened by excavation, redistribution, and mixing of the soil matrix, influenced by extensive land use changes [55]. A study in Rome examines lead, copper, nickel, and zinc concentrations in soils of urban parks and gardens, emphasizing the contribution of vehicle traffic to metal pollution and proposing mitigation measures [56]. A study on volcanic agricultural soils in southwestern Italy reveals elevated concentrations of chromium and copper due to irrigation with contaminated water, suggesting a potential risk of metal-rich sediment transfer during water movement [57]. Roman industrial mining and smelting have had a lasting impact on atmospheric contamination, with lead and copper used in water supply networks causing significant contamination in adjacent city harbors [58–62]. Investigations of abandoned sites in northern Italy with extractive wastes indicate elevated concentrations of Co, Cu, Ni, Cd, and Zn, posing significant risks to the environment and living organisms [63]. The D.Lgs 152/06 plays a crucial role in Italy by regulating the remediation of contaminated sites, outlining procedures, criteria, and methods in alignment with EU principles, particularly emphasizing the "polluter pays" principle (Gazzetta Ufficiale della Repubblica Italiana, 2006) [64].

The European Union is increasingly focusing on soil monitoring for PTEs content. In light of the increasing awareness of soil-related issues, such as the need for conservation and sustainable utilization, the European Union took a significant step on 5 July 2023 by proposing a new Soil Monitoring Law (Directorate-General for Environment, European Commission, 2023) [65]. This regulatory initiative aligns with the broader context of environmental concerns, as exemplified by numerous studies focusing on metals in the urban soils of Rome and other cities in Italy. These studies have played a crucial role in enhancing our understanding of the extent and impacts of urban soil pollution [5,35,36,54,56,57,60,63,66–73]. The regulatory standards for PTE concentrations in soil vary between countries and jurisdictions in the European Union. Although the exact reason for this obvious variability is not clear, yet different regions may have distinct geological compositions, leading to variations in background concentrations of PTE in the soil. This natural variability in geological composition can influence the establishment of regulatory standards. In addition, environmental conditions, such as climate, precipitation, and soil types, can also affect the mobility and bioavailability of PTEs, influencing the level of concern and, consequently, regulatory limits.

Soils of urban areas can be extensively exposed to PTEs because of several industrial and commercial activities, such as those related to metallurgy, mining, fossil fuels, vehicular traffic, and waste materials [5]. However, urban soils are not differentiated from other soils while framing regulatory guidelines. Thus, the regulatory limits for PTE concentrations may not be appropriate for urban soils. To overcome this limitation and to identify the hotspot soils, Serrani et al. [5] proposed a dynamic "threshold of attention" for each PTE that was obtained by adding one-half of the standard deviation to the arithmetic mean for that PTE in various study samples.

This study aimed to investigate the spatial distribution of PTEs Be, Ba, Pb, Co, Ni, V, Zn, Hg, Cd, As, Cu, and Cr in agricultural soils in the Rome (Italy) area. It focuses on the variation and spatial distribution characteristics of these PTEs at a regional scale in the urban agricultural areas of Rome, Italy, particularly in the area outside the "Grande Raccordo Anulare" (GRA) ("Great Ring Junction") where there is greater potential for using urban soils for agricultural purposes. The goal was to comprehend the established relationships between PTEs and their respective sampling locations. The research uses, besides descriptive statistics, multivariate analysis methodologies (principal component analysis (PCA) and cluster analysis) and geographic information systems (GIS). Ultimately, the study aimed to identify groups and spatial patterns of similarity in PTE concentrations/sampling locations in the soils. The findings obtained from this research could set a precedent in the particular region under examination, providing valuable insights for comparable studies in areas where agriculture, construction, and mining intersect. However, only for Ba, this study adopted the recommended threshold limit used in Portugal (210 mg/Kg) due to the non-availability of the Italian limit for Ba.

2. Materials and Methods

2.1. Study Area, Soil Sampling and Sample Preparation

Figure 1 shows the location of sampling points in the urban areas of Rome, Italy. Rome, one of the largest urban regions in the northern Mediterranean basin, spans 5363.22 km^2 with over 4.3 million inhabitants and has a population density of 788 inhabitants per km^2 [74].

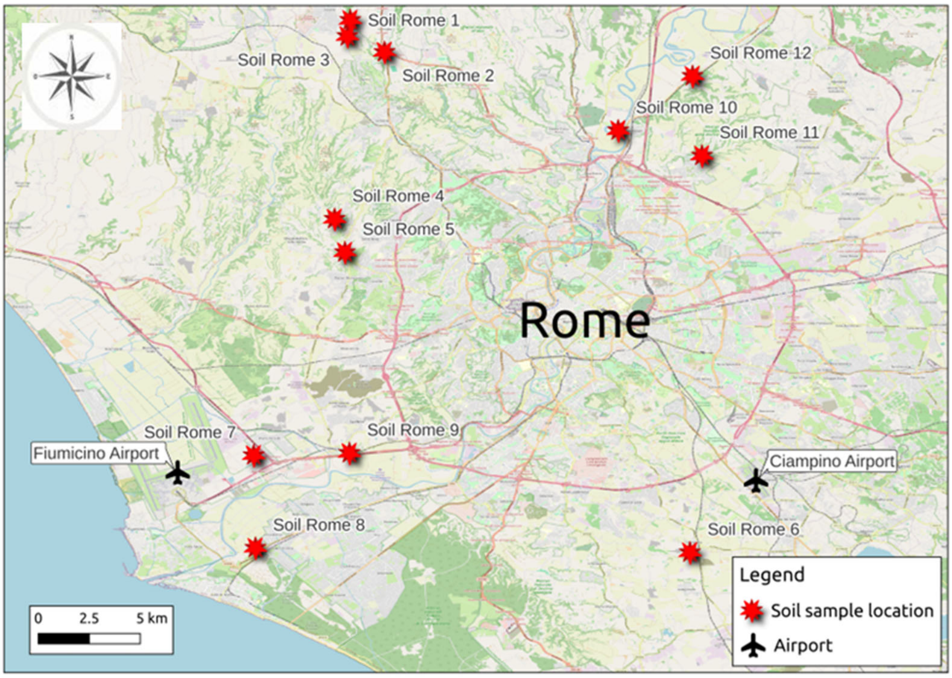


Figure 1. Study area map showing the location of soil samples collected in Rome.

As the third-largest metropolitan city in Italy, the Metropolitan City of Rome Capital encompasses nearly one-third of the Lazio region. The focus of the investigation is primarily on the Rome municipality, covering 150,061.3 ha, and specifically, the arable land within it that amounts to 49,263.97 ha (QGIS 3.34) [75]. The "Città Metropolitana di Roma (CMRC)" institution plays a crucial role in guiding the sustainable development of the metropolitan area, with a key focus on enhancing food security via strategic planning, protection of high-production areas, and promoting local supply chains [76,77]. The Rome municipality is observed as an extraordinarily rich metropolis with great historical and environmental significance having a long history of biodiversity conservation and sustainable development [78,79]. A focal point of Roman urban agriculture is the intricate examination of the historical and socio-economic dynamics that transformed the city's landscape since the 1950s, shedding light on the specific features of peri-urban agriculture and emphasizing Rome as a paradigmatic example of the urban Mediterranean city with intense interconnections between the urban and rural dimensions [79,80].

According to the climate change knowledge portal [81], the mean annual average surface air temperature for Italy during the period 1991 to 2020 has ranged from 5.28 °C in the winter (December to February) to 21.63 °C in the summer (June to August). Furthermore, the portal acknowledges that rainfall (aggregated accumulated precipitation) in Italy during the same period has ranged from 155.84 mm in the summer (June to August) to 273.90 mm in the Autumn (September to November).

In the present study, the 12 study locations for soil sampling in Italy included 44 Cesano EST VU2 (44CE.VU2), 52 Olgiata NORD VU1 (52ON.VU1), 49 Via m. Visentini VS2 (49VmV.VS2), 60 Via Cherasco VU2 (60VC.VU2), 58 Via m. Filippini GG1 (58VmF.GG1), Mongale 3 Prato Naturale IN (M3PN.IN), Ostia Antica 3 Volponi (OA3V), Ostia Antica 2 Volponi AC2 (OA2V.AC2), Mariotti 1 Ortaggi AC2 (M1O.AC2), Settebagni 5 AC2 (S5.AC2), Marcigliana 8 AN2 (M8.AN2), Tenuta Columba Salaria 1 AC3 (TCS1.AC3). The characteristics of the 12 sampling locations are described in Table 1.

Table 1. Characteristics of the 12 sampling locations.

Locations [1]	**Coordinates**	**Characteristics**
44CE.VU2	(42.07139, 12.3541)	Green space near military zone, lakes, and school faces contamination risk from urban and industrial areas, designated Special Protection Area (SPA), and near NATURA 2000, emphasizing ecological impact on flora and fauna.
52ON.VU1	(42.05254, 12.37427)	Proximity to multiple roadways exposes soil to PTEs, heightened risk in urban environment from industrial activities and vehicular emissions.
49VmV.VS2	(42.06189, 12.35241)	Dynamic urban/suburban setting exhibits varying soil characteristics influenced by historical land use, proximity to roadways, local geological conditions, vehicular emissions, and road runoff, coupled with anthropogenic alterations and nearby urban activities, emphasizing need for comprehensive analysis to assess potential PTE contamination.
60VC.VU2	(41.95411, 12.34489)	Agricultural land with olive trees and irrigation systems near main road, ideal for comprehensive PTE analysis, ensuring environmental and agricultural sustainability.
58VmF.GG1	(41.93446, 12.35094)	Landscape with agricultural crops and residential buildings near GRA ring, critical for soil analysis to understand land use impact and environmental factors on soil quality and composition.
M3PN.IN	(41.7574, 12.5543)	Situated near Ciampino airport, featuring tall trees, agricultural crops, and proximity to major roadways, provides valuable insights into the complex interplay of urban infrastructure, natural reserves, and land use practices on soil composition, with potential influences from airport-related activities, agricultural practices, and vehicular pollutants.
OA3V	(41.8147, 12.2972)	Situated near Fiumicino Airport and connected to major roadways, presents a complex environment with industrial, transportation, and agricultural activities, emphasizing the need for comprehensive soil analysis to assess potential PTE contamination risks and implications for crop quality and food safety in this intricate landscape.
OA2V.AC2	(41.7601, 12.2982)	Well-developed urban settlement near River Tiber and urban settlements with cultural landmarks, requires critical PTE analysis for preservation of environmental, historical, and public health aspects.
M1O.AC2	(41.816, 12.3536)	The sample from this field near Autostrada Roma-Fiumicino, GRA ring, and industrial zones, demands thorough PTE analysis for potential contamination risks in an urban–industrial interface.
S5.AC2	(42.00631, 12.51202)	Near Salaria Sports Village and River Tiber, essential PTE analysis needed for informing land use decisions in the urban planning area of Settebagni.
M8.AN2	(41.99146, 12.56138)	Soil sample from Via della Marcigliana within Riserva Naturale della Marcigliana necessitates PTE analysis for safeguarding historical and environmental integrity.
TCS1.AC3	(42.0384, 12.55583)	Soil sample from Via Salaria within Riserva Naturale della Marcigliana demands PTE analysis for safety of produce and environmental protection in agriculturally significant area.

[1] **Abbreviations:** CE—Cesano EST, ON—Olgiata NORD, VmV—Via m. Visentini, VC—Via Cherasco, VmF—Via m. Filippini, M3PN—Mongale 3 Prato Naturale, OA3—Ostia Antica 3 Volponi, OA2V—Ostia Antica 2 Volponi, M1O—Mariotti 1 Ortaggi, S5—Settebagni 5, M8—Marcigliana 8, TCS1–Tenuta Columba Salaria 1.

The study area consists of territory inside the boundaries of the municipality of Rome, Italy. The Urban Atlas of Rome city is a vector file representing land use (including agricultural areas) in the Metropolitan area of Rome. The agricultural land is classified under class 2 with a minimum mapping unit of 1 ha, and our target class is 21,000: arable land (annual crops) [82]. Reconstruction of the CTR mosaic (Carta Tecnica Regionale or Regional Technical Map) was performed by downloading all the raster CTR covering Rome's municipality area (the maps in the background in the soil map) (Source: Lazio

Pedological Map and Index of cartografia CTR_10K_TIF ROMA LIMITI) [83]. Subsequently, georeferencing the soil map using the EPSG of the map-EPSG 3004 and later, the digitization process was accomplished in free QGIS software for Rome by digitizing the mapped polygons. Finally, various soil types found in this region were summarized based on information from the source Carta dei Suoli del Comune di Roma in scala 1:50.000-I SUOLI DI ROMA Due passi sulle terre della città (soil map of the municipality of Rome) [84].

Selected sites within the Rome municipality, featuring diverse soil types and land uses, were identified using Google Earth and Google Maps. A comprehensive list of urban farm locations, complete with addresses, email contacts, and phone numbers, was compiled. Contact was established with these farms to seek cooperation for soil surveying, and permission from landowners was obtained for sample collection.

A total of 12 samples of agricultural soils were collected for this study in 2023 in Rome, Italy, characterized by various types of land uses such as tree cover, shrubland, grassland, cropland, and built-up area (Figure 1). Figure S1 (see Supplementary Materials) shows the spatial distribution of 12-PTE concentrations at each sample location presented against the background of Land Use Land Cover (LULC) derived–from ESA WorldCover 2021 using the v200 algorithm [85].

The maps were generated in QGIS 3.34, where the ESA WorldCover data were downloaded, clipped to the Rome region of interest, and utilized as the background. The individual PTE concentration maps were created in QGIS 3.34 [75] and subsequently merged into a single map.

At each of the sites, one composite sample (1 kg of soil), consisting of 15–20 subsamples, was taken. They were then placed in airtight polyethylene bags, labeled (with coordinates, location name, and type of cultivation), and taken to the laboratory for analysis. Soil was collected using an auger from the upper 30 cm surface layer (the depth of rooting for most plants). Basic geographic data were acquired from Google Earth and QGIS 3.34 [75].

The soils were collected in three different batches in 2023 (April, May, and July 2023). The first and second batch soils were dried at room temperature for 1–2 weeks, and the third batch soils were dried in a hot air oven at 60 °C for two days. Both air-dried and oven-dried soils were passed through a 2 mm stainless steel sieve to remove debris and stone fragments. The fine earth and stone weight after sieving were measured in a weighing balance and noted down. The fine earth was split into two halves and stored in Ziploc bags, one for immediate use in laboratory experiments and the other for future use.

2.2. Analytical Methods, Statistical Analysis, and Regulation Limits

All PTEs were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) at Eurofins Analytico B.V. according to the reference method NEN-EN-ISO 17294-2. Table 2 shows the elements analyzed and their respective Italian Law limits, A and B [64].

Descriptive statistics, encompassing measures such as the mean, maximum, minimum, median, Quartile 1, Quartile 3, skewness, kurtosis, Kolmogorov–Smirnov (K-S) test, and coefficient of variation (CV) were computed using free Software R 4.2.2 version (RStudio) [86] for the samples. The Kolmogorov–Smirnov test [87] was employed to evaluate the normality of the variable distributions, and also variability in PTE concentrations was estimated using the coefficient of variation. The average (standard deviation) of the concentration of the elements for each of the observed clusters was performed in Microsoft Excel 365.

The bar chart depicting individual PTE content in 12 sampling locations of Rome, cluster analysis, three-dimensional principal component analysis (PCA) biplot for sampling locations and PTEs, and Pearson correlation coefficient matrix for PTEs under the study were performed using the OriginPro Software 2021 version [88]. Subsequently, the two-dimensional principal component analysis (PCA) biplot for sampling locations and PTE content was performed using free Software R 4.2.2 version (RStudio) [86].

Table 2. Concentrations (mg/kg) of PTEs with their critical limits in accordance with Italian Law.

Sample/Limits	**As**	**Ba** [1]	**Be**	**Pb**	**Co**	**Cu**	**Cr**	**Ni**	**V**	**Zn**	**Hg**	**Cd**
44CE.VU2	16	**650**	**7.6**	53	14	35	9.5	18	**120**	60	nd [2]	nd
52ON.VU1	**32**	**980**	**12**	**110**	18	35	27	26	**130**	83	0.18	nd
49VmV.VS2	**28**	**950**	**11**	**110**	20	32	38	28	**140**	88	0.052	nd
60VC.VU2	**21**	**290**	**4.8**	40	6.1	15	12	12	44	29	0.24	nd
58VmF.GG1	20	**450**	**6**	51	14	19	31	24	75	41	nd	nd
M3PN.IN	**28**	160	1	**200**	20	64	51	55	34	**690**	0.12	0.55
OA3V	**23**	**740**	**4**	**1200**	16	**310**	36	40	89	120	0.43	nd
OA2V.AC2	14	**610**	**3**	91	14	48	51	46	72	91	0.25	nd
M1O.AC2	12	**340**	**2.9**	37	16	51	56	55	63	110	0.63	nd
S5.AC2	8.2	210	1.8	24	16	31	59	60	52	77	0.29	nd
M8.AN2	**24**	**1000**	**10**	99	**22**	48	39	39	**120**	83	0.091	nd
TCS1.AC3	11	**230**	**2.9**	31	16	40	73	61	74	92	0.23	nd
Limit A (residential and green public use)	**20**	**-**	**2**	**100**	**20**	**120**	**150**	**120**	**90**	**150**	**1**	**2**
Limit B (for commercial or industrial land use)	**50**	**-**	**10**	**1000**	**250**	**600**	**800**	**500**	**250**	**1500**	**5**	**15**

[1] For Barium, the Portuguese recommended limit (210 mg/kg) for residential and green public use was used for comparison. [2] nd—not detected. Potentially toxic element (PTE) concentrations exceeding the limit A are highlighted in bold. Abbreviations: CE—Cesano EST, ON—Olgiata NORD, VmV—Via m. Visentini, VC—Via Cherasco, VmF—Via m. Filippini, M3PN—Mongale 3 Prato Naturale, OA3—Ostia Antica 3 Volponi, OA2V—Ostia Antica 2 Volponi, M1O–Mariotti 1 Ortaggi, S5—Settebagni 5, M8—Marcigliana 8, TCS1—Tenuta Columba Salaria 1.

Prior to conducting PCA and cluster analysis on the PTE data, auto-scaling was applied to ensure the equal contribution of each variable, preventing dominance by variables with larger scales and enhancing the reliability of the results.

PCA was conducted to identify latent factors and reduce dimensionality, facilitating a clearer interpretation of underlying patterns in potentially toxic element concentrations across various sampling locations. Additionally, cluster analysis was employed to classify similar patterns, revealing distinct groups and providing insights into the spatial and compositional variability of PTE concentrations in the study. The Pearson correlation coefficient matrix was calculated to assess the strength and direction of linear relationships between PTEs and sampling locations, guiding further analysis into the interconnected dynamics of PTE occurrences in the studied areas.

In Italy, environmental regulations are governed by Legislative Decree 152/2006, known as the "Single Environmental Text", which consolidates laws on environmental protection [64]. This decree establishes Contamination Thresholds (CSC) for potentially toxic elements (PTEs) in soil and water [89], as outlined in the Ministerial Decree (D. Lgs. 152/06, 2006).

3. Results

3.1. Location-Wise Concentrations of PTEs

This study focused on twelve locations across metropolitan Rome (Figure 1). The concentrations of twelve PTEs were measured in each location. However, Hg and Cd did not exhibit detectable values during the analysis and were thus excluded from further analysis (descriptive statistics, principal component analysis (PCA), cluster analysis, and Pearson correlation matrix).

Figure 1 shows the GRA of Rome and the location/sites under investigation are well distributed outside GRA; location/sites M3PN.IN, OA2V.AC2, OA3V, and M1O.AC2 are close to the airports; the other eight sites are located on the north and western side of Rome.

Table 2 shows the location-wise concentrations of PTEs in the topsoil in this study and their permitted Italian limits for agricultural land use (Limit A) and commercial or industrial land use (Limit B). Since our study focused on agricultural land use, Limit A was considered the permitted limit in this study [90].

As shown in Table 2 and visualized in Figure S2, S5.AC2 was the only study location with none of the studied PTEs outside the permitted limit.

In contrast, three locations (52ON.VU1, 49VmV.VS2, and OA3V) had concentrations outside the permitted limits for any five of the twelve PTEs studied. One location (M8.AN2) had that for any four of the twelve PTEs, and three locations (44CE.VU2, 60VC.VU2, and M3PN.IN) had that for any three of the twelve PTEs. Similarly, four locations had any two or fewer PTE concentrations outside the permitted limit: 58VmF.GG1, OA2V.AC2, M1O.AC2, and TCS1.AC3. Figure S3 visualizes the spatial distribution of PTE concentrations with land use in Rome, Italy.

In terms of elevated concentrations of individual PTEs, Cr and Ni were within the permitted limit in all locations. Zn, Cu, and Co were found outside the permitted limit in one location each. In contrast, Be, As, Pb, and V were found outside the respective permitted limits in nine, six, four, and four locations, respectively. In addition, Ba was found to be outside the permitted limit for Portugal in as many as 10 out of 12 locations; however, the results for Ba need to be interpreted with caution, as Italian limits for Ba have not been defined. Furthermore, even when the concentrations of PTEs were compared against limit B, the concentrations of Be and Pb exceeded those specified in limit B in two and one study locations, respectively. Thus, at least the high concentrations of Be, As, Pb, and V in most of the studied urban soils in Rome, Italy, may be highly relevant to the public health concerns of agricultural output affected by PTE contamination.

Another way to interpret data from Table 2 could be by studying the magnitude of the increase from the permitted limits, as that may also influence the risk of hazards. In this context, greater than a 2-fold increase from the permitted limit was seen for Ba in eight locations (of which the highest concentration was 1000 mg/Kg; 4.8-fold elevation), Be in four locations (of which the highest concentration was 7.6 mg/Kg; 3.8-fold elevation), Pb in one location (1200 mg/Kg; 12-fold elevation), Cu in one location (310 mg/Kg; 2.6-fold elevation), and Zn in one location (690 mg/Kg; 4.6-fold elevation). Therefore, the extent of contamination in the locations with a greater than 2-fold elevation from the permitted limit may be highly relevant to the concern of PTE contamination of agricultural output.

In summary, Figure S3 shows the PTE concentrations across the 12 study locations.

3.2. Descriptive Statistics

Table 3 shows the descriptive statistics for the concentrations of the studied PTEs in Rome as per the combined results of all 12 study locations. In contrast, mean concentrations of three PTEs—Ba (550.83 mg/Kg), Be (5.58 mg/Kg), and Pb (170.50 mg/Kg)—exceeded the specified permitted limits for agricultural land use of 210 mg/Kg, 2 mg/Kg, and 100 mg/Kg, respectively. As for As (19.77 mg/Kg), its mean concentration nearly approached the permissible limit of 20 mg/Kg. However, the mean concentrations of the remaining PTEs were well within the specified limits for agricultural land use. In terms of median PTE concentrations, the permitted limits were exceeded by the median concentrations of As (20.50 mg/Kg), Ba (530.0 mg/Kg), and Be (4.40 mg/Kg). However, the median concentrations of lead (72.0 mg/Kg) and other studied PTEs were within the permitted limit for agricultural land use.

Table 3 also shows that the distribution of PTE concentrations in this study revealed asymmetry for several PTEs; high skewness was observed for Be (0.56), Pb (2.90), Co (−0.91), Cu (2.86), and Zn (2.90). In addition, a highly leptokurtic distribution (more peaked than the normal curve) was seen for Pb (9.64), Cu (9.53), and Zn (9.68). The coefficients of variation for the studied PTEs also showed high asymmetry in the distribution of several PTEs and were above 100% for Pb (192.37%), Cu (131.36%), and Zn (136.68%). Together, these descriptive statistics indicate a high variance among the PTE concentrations, which could be explained by the anthropogenic origin of the PTEs.

Table 3. Summary of descriptive statistics [1] for PTE contents (mg/kg) in soil samples of present study.

	As	Ba	Be	Pb	Co	Cu	Cr	Ni	V	Zn
Mean	19.77	550.83	5.58	170.50	16.01	60.67	40.21	38.67	84.42	130.33
Minimum	8.20	160.00	1.00	24.00	6.10	15.00	9.50	12.00	34.00	29.00
Q1	13.50	275.00	2.90	39.25	14.00	31.75	30.00	25.50	60.25	72.75
Median	20.50	530.00	4.40	72.00	16.00	37.50	38.50	39.50	74.50	85.50
Q3	25.00	792.50	8.20	110.00	18.50	48.75	52.25	55.00	120.00	96.50
Maximum	32.00	1000.0	12.00	1200.0	22.00	310.00	73.00	61.00	140.00	690.00
Skewness	0.03	0.25	0.56	2.90	−0.91	2.86	−0.09	−0.08	0.25	2.90
Kurtosis	1.82	1.57	1.91	9.64	4.17	9.53	2.27	1.64	1.75	9.68
K-Sp	1.00	0.85	0.87	0.04	0.56	0.04	0.98	0.90	0.79	0.02
CV [%]	38.39	57.12	66.97	192.37	25.41	131.36	47.03	43.91	41.89	136.68

[1] Q1—lower quartile; Q3—upper quartile; K–S—Kolmogorov–Smirnov; CV—coefficient of variation.

3.3. Permitted and Reported PTE Concentrations across Countries and Jurisdictions

Several regulatory standards for PTEs in soil across countries, exemplified by variations in Italy, Netherlands, MEF Finland, Germany, Portugal, Canada, and the US EPA, stem from a combination of geological distinctiveness, environmental factors, and nuanced risk assessments. Geological variations contribute to differing background concentrations of PTEs, influencing the establishment of standards. The intended land use, exposure pathways, and local priorities also play a role, leading to tailored regulations. Evolving scientific understanding, legal frameworks, and international guidelines further contribute to the complexity, reflecting a commitment to safeguarding human health and the environment within the specific context of each nation [91]. Table 4 provides a comparative overview of regulatory standards for potentially toxic elements in soil across different countries, including Italy, the United States, Finland, Germany, Netherlands, World Health Organization (WHO), Portugal and Canada. These standards are crucial for understanding the variations in environmental regulations regarding soil contamination.This study also examined the literature for the actual PTE concentrations reported by various recent studies conducted on agricultural lands and soils around the world. The results of this literature review are shown in Table 5, together with the range of concentrations observed in this work. This table shows marked variations in the concentration in soils from different origins resulting from anthropogenic and natural origin.

Notably, several studies have shown grossly high values for certain PTEs, such as Pb (1200 mg/Kg in the present study, 4265 mg/Kg in the study by Pawara [92], and 3601 mg/Kg in another study from Rome [56]), Cu (310 mg/Kg in the present study), Cr (633 mg/Kg in the study by Pawara [92] and 233 mg/Kg in another study from Turin [93]), Ni (209 mg/Kg in the study from Torino [94]), and Zn (690 mg/Kg in the present study and 996 mg/Kg in another study from Rome [56]). Interestingly, most studies with these outliers were conducted in Italy.

Table 4. Regulatory standards of PTEs in soil (mg/kg).

Organization/Country	As	Ba	Be	Pb	Co	Cu	Cr	Cd	Ni	Hg	V	Zn	Ref.
Italian Limit A (Public, private, and residential)	20	-	2	100	20	120	150	2	120	1	90	150	[64]
Italian Limit B (Commercial/Industrial use)	50	-	10	1000	250	600	800	15	500	5	250	1500	[64]
US EPA	0.11	-	-	200		270	11	0.48	72	1.0	-	1100	[95–97]
MEF, Finland	5	-	-	60	20	100	100	1	50	0.5	100	200	[18,98]
MEF, Finland (Lower guideline value)	50	-	-	200	100	150	200	10	100	2	150	250	[18,98]
MEF, Finland (Higher guideline value)	100	-	-	750	250	200	300	20	150	5	250	400	[18,98]
Germany	50	-	-	1000	-	200	500	5	200	5	-	600	[97]
Netherlands	76	-	-	530	-	190	180	13	100	36	-	720	[97]
WHO	-	-	-	0.1	-	-	0.1	0.003	0.05	−0.08	-	-	[95]
Canada Ontario (Agriculture)	(25) 20	(1000) 750	1.2	200	(50) 40	(200) 150	(10) 8.0	(4.0) 3.0	(200) 150	10	(250) 200	(800) 600	[99]
Portugal (Agriculture)	11	210	2.5	45	19	62	0.66	1	37	0.16	86	290	[90]

Elements: As—Arsenic, Ba—Barium, Be—Beryllium, Pb—Lead, Co—Cobalt, Cu—Copper, Cr—Chromium, Ni—Nickel, V—Vanadium, Zn—Zinc, Hg—Mercury, Cd—Cadmium.

Table 5. Concentrations of PTEs (mg/kg) in agricultural soils.

Region	**As**	**Ba**	**Be**	**Pb**	**Co**	**Cu**	**Cr**	**Ni**	**V**	**Zn**	**Ref.**
Rome	8.2–32	160–1000	1–12	24–1200	6.1–22	15–310	9.5–73	12–61	34–140	29–690	[1]
Moquegua	20.7	181.90	-	16.6	10.4	57.1	8.9	7.5	49.9	78.3	[100]
Lisbon	-	-	-	8.5	-	-	51.5	62.4	-	-	[48]
Łód’z	-	-	-	21.6	-	8.39	-	2.10	-	42.8	[46]
Zhejiang	14.28	-	-	40.28	-	27.95	49.01	26.97	-	-	[101]
Pawara	-	-	-	4265.0	-	122.3	633.6	-	-	128.7	[92]
Athens	29	-	-	77	16	48	163	111	-	122	[102]
Megara Plain	-	-	-	-	17.2	22.8	4.8	6.6	-	15.5	[103]
Zhongshan	17.56	-	-	50.67	-	56.81	77.20	38.31	-	131.33	[104]
Ajka	6.027	-	-	13.13	-	11.66	-	19.05	-	43.38	[105]
Cantabria	21.0	257.0	-	37.4	7.9	15.1	67.1	23.8	75.3	86.8	[106]
Campania	15.4	509	5.73	82.4	11.1	128	20.7	16.4	79.7	136	[89]
Warsaw	-	-	-	64.2	-	14.0	-	8.83	-	152	[107]
Palermo	-	-	-	202	5.2	63	34	17.8	54	138	[36]
Ancona	-	-	-	97.4	18.1	63.9	45.6	50.9	-	199.1	[5]
Torino	-	-	-	149	-	90	191	209	-	183	[94]
Salerno	10.5	304.3	4.1	126	8	75.2	19.4	16.6	56.5	197	[54]
Sopron	-	-	-	109.2	30.8	88.9	-	43.3	-	151.9	[108]
Florida	1.37	36.9	-	39.5	0.71	9.57	16.4	3.55	-	54.6	[109]
European Union (EU)	3.72	-	-	15.3	6.35	13.01	21.72	18.36	-	-	[35]
Turin	11	-	-	124	27	94	233	164	86	170	[93]
Rome	-	-	-	3601.2	-	280.1	-	97.2	-	996.0	[56]
Northern Latium	-	-	18.3	-	-	-	-	-	-	-	[68]

[1] Results obtained in this work. Elements: As—Arsenic, Ba—Barium, Be—Beryllium, Pb—Lead, Co—Cobalt, Cu—Copper, Cr—Chromium, Ni—Nickel, V—Vanadium, Zn—Zinc, Hg—Mercury, Cd—Cadmium.

3.4. Clustering of PTEs and Locations Based on Similarity

Figure 2 shows the clusters of PTEs obtained using the Pearson cluster analysis. Overall, six clusters were identified, with cluster one comprising As; cluster two including Ba, V, and Be; cluster three including Pb and Cu; cluster four comprising Co; cluster five including Cr and Ni; and cluster six comprising Zn.

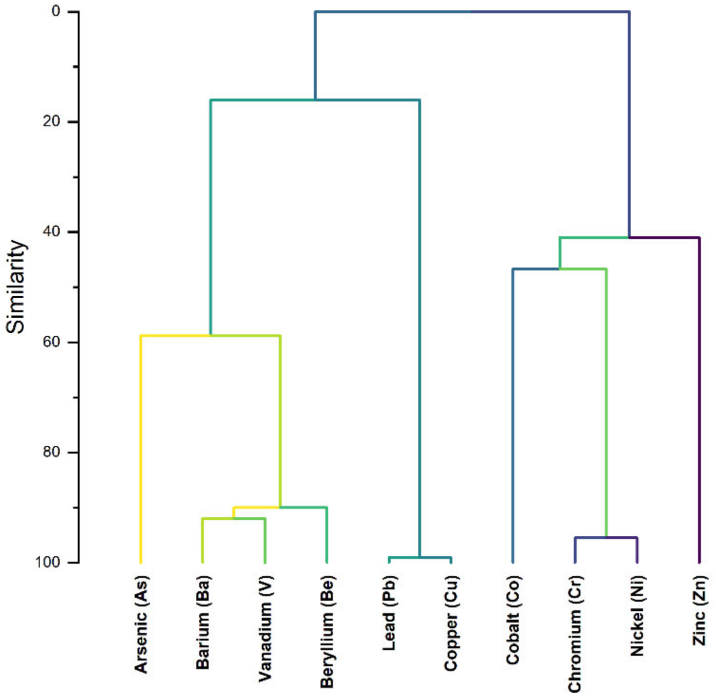


Figure 2. Pearson cluster analysis for PTEs based on similarity.

Figure 3 shows the clusters of locations obtained using the Euclidean vertical cluster analysis. A total of five clusters of locations were identified. Cluster I included three locations: 58VmF.GG1, 44CE.VU2, and OA2V.AC2. Cluster II included four locations: M1O.AC2, 60VC.VU2, S5.AC2, and TCS1.AC3. Cluster III included three locations: M8.AN2, 52ON.VU1, and 49VmV.VS2. Cluster IV included one location: M3PN.IN. Cluster V also included one location: OA3V.

The average concentrations of the PTEs in these five location clusters are shown in Table 6. The table shows that Clusters I and II had lower mean concentrations for most PTEs, while clusters III, IV, and V had higher mean concentrations for several PTEs.

Table 6. Average (standard deviation) of the concentration of the elements of the observed clusters.

Cluster *	As	Ba	Be	Pb	Co	Cu	Cr	Ni	V	Zn
I	17(3)	**570(106)**	6(2)	65(23)	14(0)	34(15)	31(21)	29(15)	89(27)	64(25)
II	13(6)	268(59)	3(1)	33(7)	14(5)	34(15)	50(26)	47(23)	58(13)	77(35)
III	**28(4)**	**977(25)**	**11(1)**	**106(6)**	**20(2)**	38(9)	35(7)	31(7)	**130(10)**	85(3)
IV	**28**	160	1	**200**	**20**	**64**	51	55	34	**690**
V	**23**	**740**	4	**1200**	16	**310**	36	40	89	**120**

* **Cluster composition:** Cluster I: 58 Via m. Filippini GG1, 44 Cesano EST VU2, Ostia Antica 2 Volponi AC2; Cluster II-Mariotti 1 Ortaggi AC2, 60 Via Cherasco VU2, Settebagni 5 AC2, Tenuta Columba Salaria 1 AC3; Cluster III-Marcigliana 8 AN2, 52 Olgiata NORD VU1, 49 Via m. Visentini VS2; Cluster IV-Mongale 3 Prato Naturale IN; Cluster V: Ostia Antica 3 Volponi.

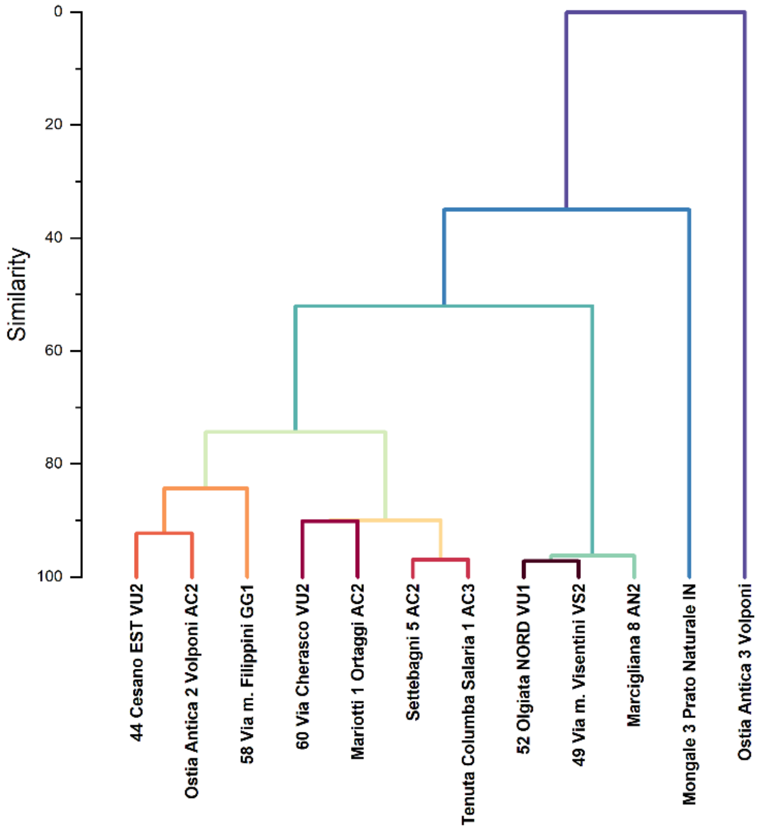


Figure 3. Pearson Euclidean vertical cluster analysis with dendrogram showing five groups of clusters based on similarity.

3.5. Principal Component Analysis to Assess the Anthropogenic Relationship between Study Locations and PTE Concentrations

Figure S4 depicts the three-dimensional principal component analysis (PCA) biplot for sampling locations and PTE concentrations, along with the PC1, PC2, and PC3 components [88], which accounted for 42%, 23.8%, and 18.3% of the variance of study results, respectively, cumulatively accounting for over 80% of the study variance. Moreover, Figure S4 indicates the anthropogenic relationship of two study locations north of Rome (Figure 1) (49VmV.VS2, and 52ON.VU1) with the high concentrations of As, Ba, Be, and V. The anthropogenic sources of heavy metals in 52ON.VU1, such as proximity to major roadways (Via di Baccanello, Via Cassia, and Via Veientana Nuova), likely contribute to soil contamination from vehicle exhaust and road maintenance activities. The urban setting, coupled with the nearby Regional Park di Veio, underscores the importance of analyzing the soil to assess the impact of urbanization and transportation on both the urban and natural environments. The anthropogenic sources near 49VmV.VS2, including a wood furnishings shop and cars servicing center near Via di Baccanello, Via Amilcare Rossi, and Via dell'Olgiatella, along with historical land use patterns and proximity to roadways like Via di Baccanello and Via Amilcare Rossi, contribute to potential heavy metal contamination in the soil via vehicular emissions, road runoff, and historical human activities. Understanding the interplay of these factors is crucial for assessing soil quality and potential risks in this urban or suburban location. In addition, the 3-D PCA also indicates the anthropogenic relationship of one study location southwest of Rome (OA3V) with the high concentrations of Cu, and Pb. The anthropogenic sources in OA3V include emissions from the nearby Fiumicino Airport, contributing heavy metals from aviation-related activities, and potential contamination from industrial and vehicular sources along major roadways like Autostrada Azzurra and Autostrada Roma-Fiumicino-Civitavecchia. The juxtaposition of industrial, transportation, and agricultural activities in the area necessitates a comprehensive analysis to assess soil quality and heavy metal contamination risks, with implications for both human health and the surrounding ecosystem. Notably, the soils of these three sites are predominantly being used as croplands, according to the data from ESA WorldCover 2021 [85].

Figure 4 depicts the two-dimensional PCA biplot for sampling locations and PTE concentrations, along with the Dim1 (42%) and Dim2 (23.8%) components; thus, the two factors (Dim1 and Dim-2) together accounted for nearly 66% of the variance in this analysis. Moreover, Figure 4 indicates the anthropogenic relationship of three study locations north of Rome (Figure 1) (M8.AN2, 49VmV.VS2, and 52ON.VU1) with the high concentrations of As, Ba, Be, and V. This analysis also indicates the anthropogenic relationship of one study location southwest of Rome (OA3V) with the high concentrations of Co, Cu, and Pb and that of another study location southeast of Rome (M3PN.IN) with the high concentrations of Cr, Ni, and Zn. The anthropogenic sources in M3PN.IN, near Ciampino airport, include potential interactions with airport-related activities, influence from agricultural practices, and pollutants from vehicular traffic along major roadways like Ferrovia Roma-Formia-Napoli ring and Via Ardeatina. Analyzing the soil in this complex environment provides insights into the interplay of urban infrastructure, natural reserves, and various land uses on soil composition and quality.

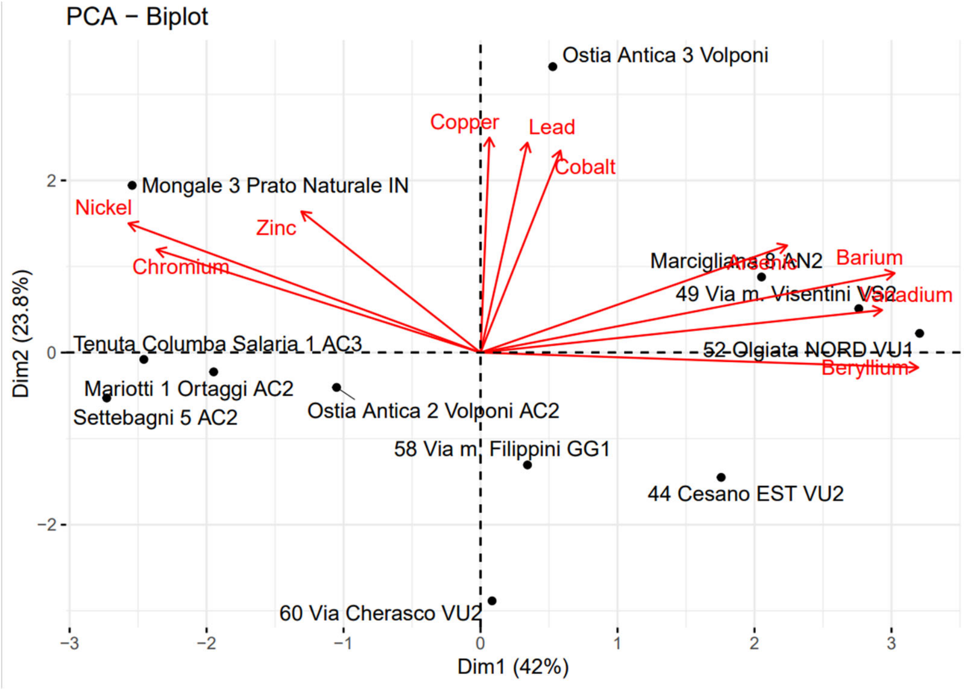
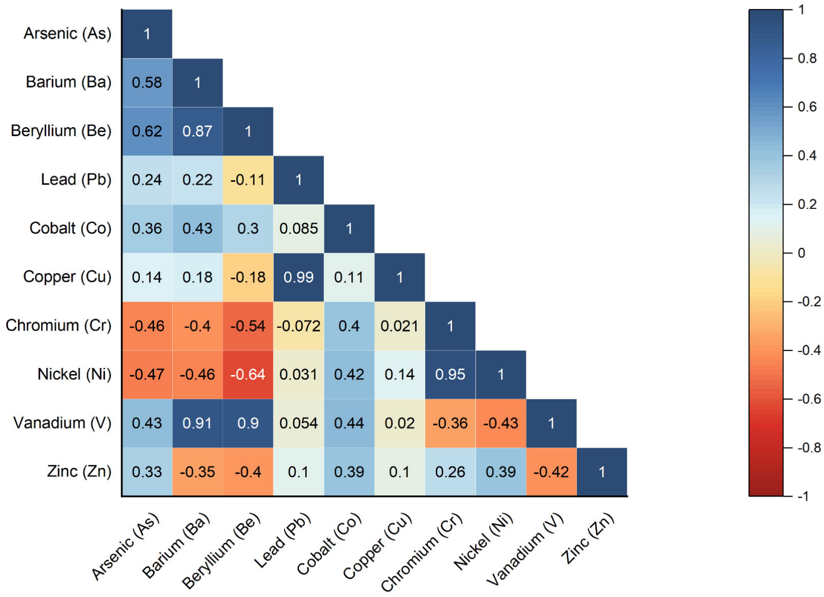


Figure 4. Two-dimensional principal component analysis (PCA) biplot for sampling locations and PTE content. Abbreviations: CE—Cesano EST, ON—Olgiata NORD, VmV—Via m. Visentini, VC—Via Cherasco, VmF—Via m. Filippini, M3PN—Mongale 3 Prato Naturale, OA3—Ostia Antica 3 Volponi, OA2V—Ostia Antica 2 Volponi, M1O—Mariotti 1 Ortaggi, S5—Settebagni 5, M8—Marcigliana 8, TCS1—Tenuta Columba Salaria 1. Elements: As—Arsenic, Ba–Barium, Be—Beryllium, Pb—Lead, Co—Cobalt, Cu—Copper, Cr—Chromium, Ni—Nickel, V—Vanadium, Zn—Zinc, Hg—Mercury, Cd—Cadmium.

Figure 5 shows the Pearson correlation coefficient matrix of the studied PTEs [88]. In this study, the five most strongly positively correlated pairs of PTEs were Cu and Pb (r = 0.99), Cr and Ni (r = 0.95), Ba and V (r = 0.91), Ba and Be (r = 0.87), and As and Be (0.62). In contrast, the five most strongly negatively correlated PTE pairs were Be and Ni (r = −0.64), Be and Cr (r = −0.54), As and Ni (r = −0.47), As and Cr (r = −0.46), and Ba and Ni (r = −0.46).



	Arsenic (As)	Barium (Ba)	Beryllium (Be)	Lead (Pb)	Cobalt (Co)	Copper (Cu)	Chromium (Cr)	Nickel (Ni)	Vanadium (V)	Zinc (Zn)
Arsenic (As)	1									
Barium (Ba)	0.58	1								
Beryllium (Be)	0.62	0.87	1							
Lead (Pb)	0.24	0.22	-0.11	1						
Cobalt (Co)	0.36	0.43	0.3	0.085	1					
Copper (Cu)	0.14	0.18	-0.18	0.99	0.11	1				
Chromium (Cr)	-0.46	-0.4	-0.54	-0.072	0.4	0.021	1			
Nickel (Ni)	-0.47	-0.46	-0.64	0.031	0.42	0.14	0.95	1		
Vanadium (V)	0.43	0.91	0.9	0.054	0.44	0.02	-0.36	-0.43	1	
Zinc (Zn)	0.33	-0.35	-0.4	0.1	0.39	0.1	0.26	0.39	-0.42	1

Figure 5. Pearson correlation coefficient matrix for PTEs under study.

4. Discussion

4.1. Contamination of Rome Topsoils

According to the present study's findings, it could be considered that the only soil S5.AC2 has no PTE toxicity among the studied soils in terms of agricultural output being at risk of PTE contamination. Further, the findings reveal a noteworthy disparity in PTE concentrations across the studied locations. Particularly, the soils from the seven distinct locations in Rome (52ON.VU1, 49VmV.VS2, OA3V, M8.AN2, 44CE.VU2, 60VC.VU2, M3PN.IN) could be considered the most un-suitable soils among the studied soils in terms of agricultural output being at risk of PTE contamination. These elevated levels of PTEs in the soil suggest a potential risk to agricultural output in these regions. Agricultural practices in soils with concentrations beyond regulatory thresholds can lead to the uptake of contaminants by crops, posing health risks to consumers and environmental challenges. Additionally, the persistence of such elevated concentrations may result in long-term soil degradation, impacting the overall sustainability of agricultural activities in these areas. The identification of these seven locations as having the most unsuitable soils among the studied samples emphasizes the urgent need for remedial measures and careful land management practices. Soil remediation strategies, such as phytoremediation or soil amendments, may be crucial to mitigate the impact of PTE contamination and restore these soils to levels compatible with safe agricultural practices.

The descriptive statistics revealed in the present study underscore a critical aspect of the PTE concentrations in Rome's soil, revealing a pronounced asymmetry and high variance among the studied elements. Specifically, the mean concentrations of Ba, Be, and Pb exceeded the permissible limits for agricultural land use, indicating potential concerns for environmental and agricultural sustainability. The notable skewness and leptokurtic distribution observed for certain PTEs, along with high coefficients of variation, suggest a complex and non-uniform spatial distribution of contaminants. This variability is indicative of anthropogenic influences on PTE concentrations in the soil, emphasizing the need for targeted mitigation strategies and continued monitoring to ensure the environmental safety of the studied locations.

The results of previous studies in Italy, alongside the observed concentrations in our study, underscore the substantial variations in soil concentrations across different origins due to both anthropogenic and natural influences. Notably, comparisons with existing studies reveal marked disparities in certain PTEs. For instance, our study found elevated values for Pb (1200 mg/Kg), Cu (310 mg/Kg), and Zn (690 mg/Kg), aligning with findings from previous research. Pawara [92] reported Pb concentrations as high as 4265 mg/Kg, while another study in Rome [56] documented values reaching 3601 mg/Kg. Similarly, our observed Cu concentration of 310 mg/Kg corresponds to Pawara's [92] findings and aligns with the study in Turin [93], where Cr concentrations reached 233 mg/Kg. Furthermore, our Ni concentration of 209 mg/Kg concurs with the study from Torino [94]. Remarkably, Italy emerges as a region with several studies reporting grossly high values for these PTEs. The notable presence of outliers in multiple studies conducted in Italy warrants further investigation into the localized factors contributing to these heightened concentrations. This comparative analysis emphasizes the need for a nuanced understanding of regional variations in PTE concentrations and their potential implications for environmental and human health.

The principal component analysis (PCA) biplots offer a comprehensive view of the anthropogenic relationships between study locations and concentrations of potentially toxic elements (PTEs). In the present study, the elevated concentrations of As, Ba, Be, and V in north Rome locations suggest anthropogenic sources, with 52ON.VU1 being influenced by proximity to major roadways and urban settings, emphasizing the need to assess the impact of urbanization and transportation on soil quality. The concentration patterns of Cu and Pb in OA3V, indicate a clear anthropogenic relationship attributed to the nearby Fiumicino Airport and industrial activities along major roadways. The juxtaposition of industrial, transportation, and agricultural activities necessitates a comprehensive analysis to understand potential heavy metal contamination risks, with implications for human health and the ecosystem. Additionally, it underscores the distinctive patterns in PTE concentrations for southwest Rome (OA3V), with Co, Cu, and Pb, and South-East Rome (M3PN.IN) with Cr, Ni, and Zn. The anthropogenic sources in M3PN.IN, including interactions with airport-related activities and vehicular traffic, underscore the complexity of urban infrastructure, natural reserves, and various land uses influencing soil composition and quality. Overall, these PCA results provide valuable insights into the anthropogenic influences on PTE concentrations in the studied locations, highlighting the need for targeted assessments considering urbanization, industrial activities, transportation, and historical land use patterns for effective soil management and environmental protection.

The Pearson correlation coefficient matrix of the studied PTEs reveals intriguing patterns of correlation among the elements. Notably, the pair of Cu and Pb demonstrates an exceptionally strong positive correlation ($r = 0.99$). This correlation is of particular interest due to the significantly elevated concentrations of both Cu and Pb observed in one study location, namely OA3V with a Cu concentration of 310 mg/Kg (against the permitted limit of 120 mg/Kg) and a Pb concentration of 1200 mg/Kg (against the permitted limit of 100 mg/Kg). The co-occurrence of heightened levels in both Cu and Pb suggests a potential common source or shared influencing factors contributing to the increased concentrations of these PTEs in the soil. This finding emphasizes the importance of examining correlations not only as statistical associations but also as valuable indicators for understanding the interplay of PTEs in specific locations. Further investigation into the causal factors behind this correlation could provide valuable insights for targeted remediation strategies and land management practices in areas where such high concentrations are observed.

4.2. Soil Standards for Urban Areas and the Need to Identify Hotspots

In this study, in addition to the permitted regulatory limit (Limit A) [64], we used the "Q3 value" for the PTE concentrations to identify hotspot soils and labeled the locations with PTE concentrations beyond the Q3 concentrations as "worthy of further scrutiny" (Box 1). Therefore, among all studied clusters, clusters 3, 4, and 5 contained the most hotspot soils for most of the studied PTEs. These results suggest that there is a need to reexamine the soil standards for urban soils in the context of high PTE concentrations bioavailability, and a systematic approach to defining hotspots is necessary to limit the unwanted public health impacts of PTE pollution.

Box 1. Hotspot Study locations considered “worthy of further scrutiny” for evaluated PTEs

As (Q3: 25.00 mg/Kg): two locations of cluster 3 and the sole location of cluster 4 were found to be worthy of scrutiny.
Ba (Q3: 792.50 mg/Kg) and **Be** (Q3: 8.20 mg/Kg): all three locations of cluster 3 were found to be worthy of scrutiny.
Pb (Q3: 110.00 mg/Kg): the sole locations of clusters 4 and 5 were found to be worthy of scrutiny.
Co (Q3: 18.50 mg/Kg): one location of cluster 3 and the sole locations of clusters 4 and 5 were found to be worthy of scrutiny.
Cu (Q3: 48.75 mg/Kg): one location of cluster 2 and the sole locations of clusters 4 and 5 were found to be worthy of scrutiny.
Cr (Q3: 52.25 mg/Kg) and **Ni** (Q3: 55.00 mg/Kg): three and two locations of cluster 2, respectively, were found to be worthy of scrutiny.
V (Q3: 120.00 mg/Kg): two locations of cluster 3 were found to be worthy of scrutiny.
Zn (Q3: 96.50 mg/Kg): one location of cluster 2 and the sole locations of clusters 4 and 5 were found to be worthy of scrutiny.

4.3. Anthropogenic and Geogenic Contributions to PTE Enrichment of Soil

Whether these hotspot soils with unusually high PTE concentrations are anthropogenic or geogenic (volcanic) can be debated because of the mixed results of earlier studies [110] and considering the origin of Roman soils from volcanic rocks [23]. Volcanic soils can be naturally expected to contain a relatively higher concentration of PTEs than non-volcanic soils [111]. However, the results from various analyses used in this study also support an important anthropogenic contribution to the high PTE concentrations found in most of the hotspots. First, during the descriptive analysis for PTE concentrations in Rome, (1) high skewness was observed for Be, Pb, Co, Cu, and Zn; (2) highly leptokurtic distribution was seen for Pb, Cu, and Zn; and (3) coefficients of variation for Pb, Cu, and Zn were above 100%. Second, five clusters of study locations were revealed in the Euclidean vertical cluster analysis. Third, in the three-dimensional PCA, two study locations were associated with high concentrations of As, Ba, Be, and V, while one study location was associated with high concentrations of Cu and Pb; the two-dimensional PCA showed consistent results with the three-dimensional PCA. Fourth, in the Pearson correlational matrix analysis, several pairs of PTEs were strongly positively correlated, including the pairs of Cu and Pb, Cr and Ni, Ba and V, Ba and Be, and As and Be; in line with this, the Pearson cluster analysis also showed six clusters of PTEs.

Taken together, these analyses indicate that anthropogenic factors are closely involved in the high concentrations of PTEs in this study. Several prior studies have also used these analyses to confirm the anthropogenic causes of high PTE concentrations in the soils [46,48,100]. A study from Rome by Calace et al. [56] also found that an anthropogenic cause (vehicular traffic) was associated with high concentrations of Cu, Ni, Pb, and Zn in the soils of parks and gardens in Rome. Other studies from different regions of Italy have also corroborated the effects of anthropogenic activities on PTE concentrations. For instance, in southern Italy (Solofrana River valley), a study has found high concentrations of Cr and Cu in agricultural soils [57]. Another study from Torino, Italy, found high concentrations of Cu, Pb, and Zn within the city’s soils [94]. In general, the PTE concentrations reported in the present study were largely consistent with the previous studies from Italy [5,89,94].

The results of the present study were also compared with those from Europe, the United States, Asia, and Africa (Table 3). In general, the PTE concentrations reported by studies from Italy, including the present study, tended to be higher than those reported from outside Italy, although Spain and Cameroon were notable exceptions. These results reiterate the contribution of the geogenic volcanic soils to the high PTE concentrations in the volcanic soils of Italy. Therefore, based on the results of the present study and the literature review, it can be suggested that the presence of volcanic soils makes Italy’s soils richer in PTEs compared to countries with non-volcanic soils (especially in Ba, Be, and V), the human factors in the cities of Italy still contribute to the additional enrichment of the soil in certain PTEs (Cu, Pb, Zn, etc.) which manifests as unusual clustering of those PTEs in certain locations.

4.4. Suitability of the Studied Soils for Urban Agriculture

The multifunctional urban agriculture initiatives in Rome, particularly those undertaken by young farmers via programs like “Rome Cultivating the City” (Roma Città da Coltivare) and “Terre ai giovani” (Lands for Youth), not only contribute to sustainable agricultural practices but also serve as effective solutions to urban sprawl, offering ecological services, biodiversity enhancement, and green connectivity while addressing socio-economic challenges. These projects showcase the potential for urban agriculture to play a pivotal role in reshaping urban-rural dynamics, fostering environmental resilience, and providing valuable ecosystem services in heavily urbanized areas [79].

The emergence of new forms of urban agriculture (NFUA), encompassing urban farms, community-supported agriculture, allotment gardens, and agricultural parks, globally signifies a strategic response to address local food demand, protect farmlands from urbanization, and enhance the cultural well-being of urban residents in contemporary metropolitan landscapes [112].

Indeed, the introduction of urban agriculture, mainly by reusing abandoned or non-productive land, involving local populations, is an important factor with great social, environmental, and economical relevance, with a strong contribution to city sustainability. However, as a consequence of decades of land occupation with industrial activities that operated without appropriate environmental regulation and the emission of diffused pollution due to cars, soils may have become with increased contaminations that may limit its utilization. This is particularly critical when food is to be produced, which may become a source of toxic substances in animal and human bodies.

In the case of the present study, besides anthropogenic pollution sources, the quality of the soils becomes compromised due to natural geologic factors. Indeed, the volcanic origin of soils contributes to relatively high levels of barium, beryllium, arsenic, and vanadium, and taking into consideration the great toxicity of some of these PTEs, the human health risks of using these soils for food production become too high. However, further information should be obtained about the bioavailability and potential transference mechanisms into the products that are being produced in those soils.

5. Conclusions

In conclusion, this study collectively underscores the critical importance of addressing soil contamination, particularly in urban environments, for effective environmental management and public health. The distinctions between point sources and diffuse pollution, the comprehensive analysis of PTE content, and the global applicability of standards highlight the complexity and urgency of the issue. The interplay of urbanization with soil properties and the potential impact on human health via the food chain emphasizes the interconnectedness of environmental and human well-being. The research also stresses the need for reliable data, comprehensive studies, and cohesive policies to guide interventions and future research. Overall, the findings contribute valuable insights for soil management, environmental health, and the development of unified strategies to mitigate the risks associated with soil contamination.

To reiterate, only one studied soil, S5.AC2 met the limit A concerning all the PTEs analyzed. The soil from OA3V was found unsuitable for both agricultural and commercial or industrial purposes because it had 1200 mg/Kg of Pb. Similarly, the soil from two locations (52ON.VU1 and 49VmV.VS2) was also unsuitable for both agricultural and industrial or commercial purposes, as the concentration of Be exceeded the respective limit B in these locations. Moreover, several locations were found to have very high concentrations that are worthy of scrutiny and detailed studies. Although the results of this study are limited by a small number of study locations and samples, these results indicate that high PTE content can be a significant barrier to the utilization of urban agricultural lands in

Rome. These results may hold great importance for cities based in volcanic soils and in industrial cities utilizing urban agricultural lands for food and feed. Further research is needed to understand the impact of soil enrichment with PTEs on agricultural output and public health.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/environments11020034/s1. Figure S1: Map showing spatial distribution of PTE content with the Land Use/Land Cover (LULC) from ESA WorldCover 2021 in the background. Figure S2: Map showing the locations having PTE content exceeding or within the limit for agriculture; as there was no limit for Barium in Italy, the limit of Portugal is used. Figure S3: PTE content among the 12 sampling locations in Rome, Italy. Figure S4: Three-dimensional principal component analysis (PCA) biplot for sampling locations and PTEs showing PC1, PC2 and PC3 components.

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