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Article

Metal Concentrations in Topsoils of Urban Agricultural Areas of Rome

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Abstract: Urban gardens have important social, environmental and economic roles in big cities, contributing to their sustainability. However, food production in urban gardens 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 metals 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 metal concentration above the threshold limit defined by the Italian Legislative Decree 152/2006 (ILD) for agricultural soils. Multivariate analysis showed that the soils could be classified into five clusters: clusters I and II had relatively lower mean metal concentrations; clusters III, IV, and V had relatively higher mean metal concentrations with several metal concentrations above the threshold proposed by ILD. Three factors contributing to the variability of the metal's concentration in the soils under investigation were identified: geological factor, related with metals As, Ba, Be, and V; anthropogenic factor, related with Pb and Cu; and, a mixed factor related with Co, Cr, Ni, and Zn. High metal content may limit the utilization of urban soils as urban gardens for food production.

Keywords: Rome soils; urban soils; urban garden; metal ions; soil pollution; multivariate analysis

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 metal pollution in urban soils is evident, with key contributors including 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. This innovative approach acknowledges the dynamic nature of urban soil pollution, offering potential solutions for effective environmental management. The World Health Organization (WHO) has identified arsenic, lead, mercury, and cadmium as major public health concerns due to their toxicity, persistence, and bioaccumulative properties [14,15]. Various anthropogenic activities contribute to the presence of these metals in urban environments, including industrial processes, soil pollution, landfills, tailings ponds, and the use of agricultural fertilizers and pesticides [15–17]. Triassi et al. [15]

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address the contamination of groundwater by metals in Southern Italy, shedding light on the environmental impacts of local industries, agriculture, and urban activities. 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) [18].

Despite a global lack of comprehensive data on metal contamination, Tóth et al. [19] conducted a detailed analysis of metal content in agricultural topsoils across the European Union. Their study emphasizes the need for targeted monitoring and remediation actions based on specific regions' risks. In their findings, they identified the Finnish standards for contaminated soil (Ministry of the Environment — MEF, Finland, 2007) [20] align closely with various national systems in Europe [21] and India [22], serving as global benchmarks for agricultural soils [23].

As developing countries undergo swift urbanization and industrialization, there is a significant influx of organic and inorganic pollutants into urban environments, posing risks to human health. With a growing urban population, the entry of metals into human bodies through multiple exposure pathways becomes a critical concern, emphasizing the need for precise risk characterization in health assessments [24,25]. Urban areas cover about 6% of Europe's total area, with 52% of the global population residing in urban or peri-urban regions [26–28]. The dynamic nature of urban environments, influenced by construction, use, and renewal processes, highlights the significant impact on urban landscapes [28,29]. The complexity of urban soils, influenced by various factors like construction remnants and drainage processes, challenges conventional assessment methods [27,30]. Agricultural practices, including prolonged flooding, terracing, and deep ploughing also impact soils, with altered soils, resulting from human-induced changes exhibiting mixing and the presence of anthropogenic horizons [28,30].

The presence of pollutants, especially metals, in landfill leachate poses a serious threat to public health and ecosystems [31–34]. Soil, as the ultimate sink for metals, accumulates these pollutants through interactions with inorganic and organic matter [34]. Heavy metals (Cd, Ba, Hg, and Pb) have the potential to enter the food chain, posing health risks through consumption, dermal contact, ingestion, and inhalation [34–36], whereas toxic metals (Cr, Mn, Cu, As) through drinking water and inhalation of soil particles [34,37,38].

In Europe, metal contamination is a significant concern, with an estimated 2.5 million potentially contaminated sites [39]. The LUCAS Topsoil Survey provides a detailed overview of metal concentrations in the topsoil of the European Union, supporting local assessments and potential control measures [40,41]. A comprehensive study on Palermo's urban soils investigated mineralogy, geochemistry, and concentrations of 11 heavy metals, offering insights into metal sources and contamination [42–44]. Peri-urban agriculture, situated between urban and rural zones, plays a pivotal role in global urban development [45,46]. However, metal contamination in peri-urban agricultural soils poses health risks for adults and children in vegetable production, as revealed by a recent meta-analysis [47]. The challenges of soil pollution in urban areas, driven by industrialization, urbanization, and transportation, necessitate quick and simple methods for assessing urban soil quality [48–52]. The recognition of Technosols as Soil of the Year 2020, characterized by strong human influence, adds significance to understanding urban soil dynamics [53]. 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 [54–57].

Recent data from the Rapid Alert System for Food and Feed (RASFF) database highlights 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 as the second most commonly involved "country of origin" [58]. A chapter on soil governance in the European Union critiques existing strategies and advocates for a unified EU soil protection framework [59]. Using the fractal/multifractal method, a study maps potentially toxic elements distribution in Salerno, offering insights for enhanced environmental management [60]. The spatial diversity of urban soils is heightened by excavation, redistribution, and mixing of the soil matrix, influenced by extensive land use changes [61]. 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 [62]. 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 [63]. Roman industrial mining and smelting have had a lasting impact on atmospheric contamination, with lead and copper use in water supply networks causing significant contamination in adjacent city harbours [64–68]. 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 [69]. The Legislative Decree 3 April 2006, n. 152, 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) [70].

On July 5, 2023, the European Union proposed a new Soil Monitoring Law to safeguard and restore soils, ensuring sustainable utilization (Directorate-General for Environment, European Commission, 2023) [71]. Numerous studies on metals in the urban soils of Rome and other cities in Italy contribute to our understanding of the extent and impacts of urban soil pollution [5,41,42,60,62,63,66,69,72–79].

This study aimed to investigate the spatial distribution of metals Be, Ba, Pb, Co, Ni, V, Zn, Hg, Cd, As, Cu and Cr in agricultural soils in the Rome (Italy) area. It focusses on the variation and spatial distribution characteristics of these metals 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 urban gardens implementation. The goal was to comprehend the established relationships between metals 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 metal 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.

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 among the largest urban regions in the northern Mediterranean basin, spans 5,363.22 km^2 with over 4.3 million inhabitants, has a population density of 788 inhabitants per km^2 [80].

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 Rome municipality, covering 150,061.3 ha, and specifically, the arable land within it amounts to 49,263.97 ha (QGIS 3.34) [81]. 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 through strategic planning, protection of high-production areas, and promoting local supply chains [82,83]. 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 [84,85]. 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 [85,86].

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

According to the climate change knowledge portal [87], 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). Further, 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).

The characteristics of the 12 sampling locations are as follows:

44 Cesano EST VU2 (GPS: 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; 52 Olgiata NORD VU1 (42.05254, 12.37427) - Proximity to multiple roadways exposes soil to metals, heightened risk in urban environment from industrial activities and vehicular emissions.**49 Via m. Visentini 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, emphasizes need for comprehensive analysis to assess potential metal contamination; **60 Via Cherasco VU2** (41.95411, 12.34489) - Agricultural land with olive trees and irrigation systems near main road, ideal for comprehensive metal analysis, ensuring environmental and agricultural sustainability; 58 Via m. Filippini 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.

Mongale 3 Prato Naturale 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; **Ostia Antica 3 Volponi** (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 metal contamination risks and implications for crop quality and food safety in this intricate landscape.

Ostia Antica 2 Volponi AC2 (41.7601, 12.2982) - Well-developed urban settlement near River Tiber and urban settlements with cultural landmarks, requires critical metal analysis for preservation of environmental, historical, and public health aspects; **Mariotti 1 Ortaggi AC2** (41.816, 12.3536) - The sample from this field near Autostrada Roma-Fiumicino, GRA ring, and industrial zones, demands thorough metal analysis for potential contamination risks in an urban-industrial interface; **Settebagni 5 AC2** (42.00631, 12.51202) - Near Salaria Sports Village and River Tiber, essential metal analysis needed for informing land use decisions in the urban planning area of Settebagni; **Marcigliana 8 AN2** (41.99146, 12.56138) - Soil sample from Via della Marcigliana within Riserva Naturale della Marcigliana necessitates metal analysis for safeguarding historical and environmental integrity; **Tenuta Columba Salaria 1 AC3** (42.0384, 12.55583) - Soil sample from Via Salaria within Riserva Naturale della Marcigliana demands metal analysis for safety of produce and environmental protection in agriculturally significant area.

The study area consists of territory inside the boundaries of municipality of Rome, Italy. 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 minimum mapping unit of 1 ha and our target class is 21000: Arable land (annual crops) [88]. 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) [89]. Subsequently, georeferencing the soil map using the EPSG of the map-EPSG 3004 and later, digitization process was accomplished in free QGIS software for Rome by digitizing the mapped polygons. Finally, various soil types found in this region were summarised 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 municipality of Rome) [90].

Selected sites within 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, built-up area (Figure 1). Figure S1 shows the spatial distribution of 12-metal concentrations at each sample location presented against the background of Land Use Land Cover (LULC) derived from ESA WorldCover 2021 using the v200 algorithm [91].

The maps were generated in QGIS 3.34, where the ESA WorldCover data was downloaded, clipped to the Rome region of interest, and utilized as the background. The individual metal concentration maps were created in QGIS 3.34 [81] and subsequently merged into a single map.

At each of the sites, one composite sample (1 kg of soil), consisting of 15–20 sub-samples, was taken. They were then placed in airtight polyethylene bags, labelled (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 was acquired from the Google Earth and QGIS 3.34 [81]. Soil samples were thus collected at 0-30 cm depth.

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 third batch soils were dried in 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, stone fragments. The fine earth and stone weight were after sieving were measured in a weighing balance and noted down. The fine earth was split into two halves and stored into Ziploc bags, one for immediate use in laboratory experiments and other for future use.

2.2. Analytical methods, Statistical analysis and Regulation limits

All metals were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) at Eurofins Analytico B.V. according to the reference method NEN-EN-ISO 17294-2. Table 1 shows the elements analyzed and their respective Italian Law limits A and B [70].

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

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variation (CV) were computed using free Software R 4.2.2 version (RStudio) [92] for the samples. The Kolmogorov-Smirnov test [93] was employed to evaluate the normality of the variable distributions and also variability in metal concentrations was estimated using the coefficient of variation. 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 metal content in 12 sampling locations of Rome, Cluster Analysis, 3-Dimensional Principal Component Analysis (PCA) Biplot for sampling locations and metals, Pearson Correlation Coefficient Matrix for metals under the study were performed with the OriginPro Software 2021 version [94]. Subsequently, the 2-Dimensional Principal Component Analysis (PCA) Biplot for sampling locations and metal content was performed using free Software R 4.2.2 version (RStudio) [92].

Prior to conducting PCA and Cluster Analysis metal data, auto scaling was applied to ensure 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's 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 metal concentrations in the study. The Pearson Correlation Coefficient Matrix was calculated to assess the strength and direction of linear relationships between metals and sampling locations, guiding further analysis into the interconnected dynamics of metal occurrences in the studied areas.

Table 1. Concentrations (mg/kg) of metals with their critical limits in accordance with Italian Law.

Sample/Limits	As	Ba[1]	Be	Pb	Co	Cu	Cr	Ni	V	Zn	Hg	Cd
44 Cesano EST VU2	16	650	7.6	53	14	35	9.5	18	120	60	nd[2]	nd
52 Olgiata NORD VU1	32	980	12	110	18	35	27	26	130	83	0.18	nd
49 Via m. Visentini VS2	28	950	11	110	20	32	38	28	140	88	0.052	nd
60 Via Cherasco VU2	21	290	4.8	40	6.1	15	12	12	44	29	0.24	nd
58 Via m. Filippini GG1	20	450	6	51	14	19	31	24	75	41	nd	nd
Mongale 3 Prato Naturale IN	28	160	1	200	20	64	51	55	34	690	0.12	0.55
Ostia Antica 3 Volponi	23	740	4	1200	16	310	36	40	89	120	0.43	nd
Ostia Antica 2 Volponi AC2	14	610	3	91	14	48	51	46	72	91	0.25	nd
Mariotti 1 Ortaggi AC2	12	340	2.9	37	16	51	56	55	63	110	0.63	nd
Settebagni 5 AC2	8.2	210	1.8	24	16	31	59	60	52	77	0.29	nd
Marcigliana 8 AN2	24	1000	10	99	22	48	39	39	120	83	0.091	nd
Tenuta Columba Salaria 1 AC3	11	230	2.9	31	16	40	73	61	74	92	0.23	nd
Limit A	**20**	**-**	**2**	**100**	**20**	**120**	**150**	**120**	**90**	**150**	**1**	**2**
Limit B	**50**	**-**	**10**	**1000**	**250**	**600**	**800**	**500**	**250**	**1500**	**5**	**15**

[1]For Barium the Portuguese recommended limit (210 mg/kg) was used for comparison. [2] nd –not detected.

PCA was conducted to identify latent factors and reduce dimensionality, facilitating a clearer interpretation of underlying patterns in potentially toxic element's 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 metal concentrations in the study. The Pearson Correlation Coefficient Matrix was calculated to assess the strength and direction of linear relationships between metals and sampling locations, guiding further analysis into the interconnected dynamics of metal 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 [70]. This decree establishes Contamination Thresholds (CSC) for potentially toxic elements (PTEs) in soil and water [95], as outlined in the Ministerial Decree (D. Lgs. 152/06, 2006). The legislation, organized into six parts, covers various environmental aspects, including strategic and environmental assessments, soil

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protection, waste management, air quality, and the precautionary principle. The overarching goal is to enhance human life quality by safeguarding the environment and ensuring the responsible use of natural resources, providing a comprehensive framework for assessing metal concentrations in compliance with established thresholds.

3. Results

3.1. Location-wise concentrations of metals

This study focused on twelve locations across metropolitan Rome (Figure 1). The concentrations of twelve metals 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 Mongale 3 Prato Naturale IN, Ostia Antica 2 Volponi AC2, Ostia Antica 3 Volponi and Mariotti 1 Ortaggi AC2 are close to the airports; the other eight sites are located on the North and Western side of Rome.

Table 1 shows the location-wise concentrations of metals 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. However, only for Ba, this study adopted the recommended threshold limit used in Portugal (210 mg/Kg) [96] due to the non-availability of the Italian limit for Ba.

As shown in Table 1 and visualised in Figure 2, "Settebagni 5 AC2" was the only study location with none of the studied metals outside the permitted limit. It could be thus considered that the soil has no metal toxicity, among the studied soils in terms of agricultural output being at risk of metal contamination

In contrast, three locations ("52 Olgiata NORD VU1", "49 Via m. Visentini VS2", and "Ostia Antica 3 Volponi") had concentrations outside the permitted limits for five metals, one location ("Marcigliana 8 AN2") had that for four metals, and three locations ("44 Cesano EST VU2", "60 Via Cherasco VU2", and "Mongale 3 Prato Naturale IN") had that for three metals. Thus, the soils from these seven locations in Rome could be considered the most unsuitable soils among the studied soils in terms of agricultural output being at risk of metal contamination. Similarly, four locations had two or fewer metal concentrations outside the permitted limit: "58 Via m. Filippini GG1", "Ostia Antica 2 Volponi AC2", "Mariotti 1 Ortaggi AC2", and "Tenuta Columba Salaria 1 AC3". Figure 3 visualizes the spatial distribution of metal concentrations with land use in Rome, Italy.

In terms of elevated concentrations of individual metals, 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 metals 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 metal contamination.

Another way to interpret data from Table 1 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 metal contamination of agricultural output.

In summary, Figure 3 shows the metal concentrations across the 12 study locations.

Figure 2. Map showing the locations having metal content exceeding or within the limit for agriculture, as there was no limit for Barium in Italy, the limit of Portugal is used.

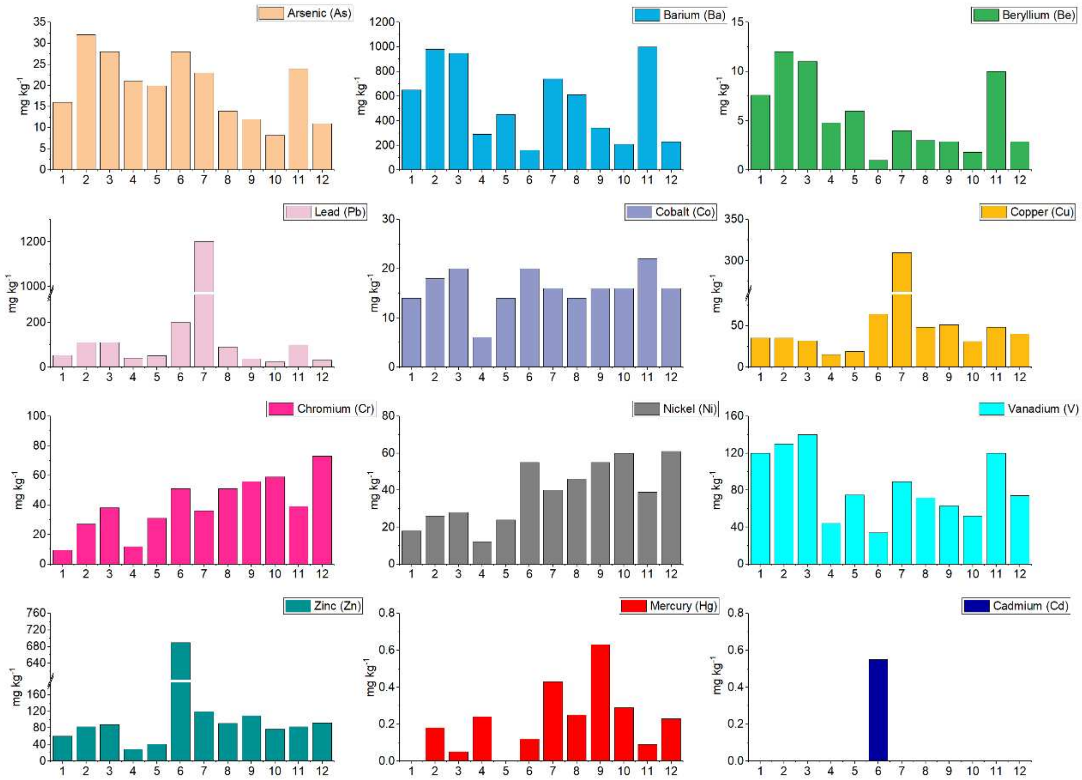

Figure 3. Metal content among the 12 sampling locations in Rome, Italy.

3.2. Descriptive statistics

Table 2 shows the descriptive statistics for the concentrations of the studied metals in Rome as per the combined results of all 12 study locations. The mean concentrations of three metals, 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. However, the mean concentration of As (19.77 mg/Kg) nearly approached the permitted limit of 20 mg/Kg. For other metals, the mean concentrations were well within the respective permitted limits. In terms of median metal 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 metals were within the permitted limit for agricultural land use.

Table 2 also shows that the distribution of metal concentrations in this study showed asymmetry for several metals; 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 metals also showed high asymmetry in the distribution of several metals 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 metal concentrations, which could be explained by the anthropogenic origin of the metals.

Table 2. Summary of descriptive statistics [1] for metal 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

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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 metals concentrations across countries and jurisdictions

For comparison between geographies and studies, this section examined the published literature for the legally regulated metal concentrations in various jurisdictions and countries, the results of which are shown in Table 3.

Table 3 shows obvious variability in regulatory standards for metal concentrations in soil between countries and jurisdictions. Though the exact reason for this variation is not clear, different regions may have distinct geological compositions, leading to variations in background concentrations of metals in the soil. This natural variability 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 metals, influencing the level of concern and, consequently, regulatory limits.

Several regulatory standards for metals 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 metals, 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 [97].

This study also examined the literature for the actual metal 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 4 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 metals, such as Pb (1200 mg/Kg in the present study, 4265 mg/Kg in the study by Pawara [98], and 3601 mg/Kg in another study from Rome [62]), Cu (310 mg/Kg in the present study), Cr (633 mg/Kg in the study by Pawara [98] and 233 mg/Kg in another study from Turin [99]), Ni (209 mg/Kg in the study from Torino [100]) and Zn (690 mg/Kg in the present study and 996 mg/Kg in another study from Rome [62]). Interestingly, most studies with these outliers were conducted in Italy.

Table 3. Regulatory standards of metals 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	[70]
Italian Limit B (Commercial/Industrial use)	50	-	10	1000	250	600	800	15	500	5	250	1500	[70]
US EPA	0.11	-	-	200		270	11	0.48	72	1.0	-	1100	[101–103]
MEF, Finland	5	-	-	60	20	100	100	1	50	0.5	100	200	[19,20]

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MEF, Finland (Lower guideline value)	50	-	-	200	100	150	200	10	100	2	150	250	[19,20]
MEF, Finland (Higher guideline value)	100	-	-	750	250	200	300	20	150	5	250	400	[19,20]
Germany	50	-	-	1000	-	200	500	5	200	5	-	600	[103]
Netherlands	76	-	-	530	-	190	180	13	100	36	-	720	[103]
WHO	-	-	-	0.1	-	-	0.1	0.003	0.05	- 0.08	-	-	[101]
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	[104]
Portugal (Agriculture)	11	210	2.5	45	19	62	0.66	1	37	0.16	86	290	[96]

Table 4. Concentrations of metals (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	[105]
Lisbon	-	-	-	8.5	-	-	51.5	62.4	-	-	[54]
Łód´z	-	-	-	21.6	-	8.39	-	2.10	-	42.8	[52]
Zhejiang	14.28	-	-	40.28	-	27.95	49.01	26.97	-	-	[106]
Pawara	-	-	-	4265.0	-	122.3	633.6	-	-	128.7	[98]
Athens	29	-	-	77	16	48	163	111	-	122	[107]
Megara Plain	-	-	-	-	17.2	22.8	4.8	6.6	-	15.5	[108]
Zhongshan	17.56	-	-	50.67	-	56.81	77.20	38.31	-	131.33	[109]
Ajka	6.027	-	-	13.13	-	11.66	-	19.05	-	43.38	[110]
Cantabria	21.0	257.0	-	37.4	7.9	15.1	67.1	23.8	75.3	86.8	[111]
Campania	15.4	509	5.73	82.4	11.1	128	20.7	16.4	79.7	136	[95]
Warsaw	-	-	-	64.2	-	14.0	-	8.83	-	152	[112]
Palermo	-	-	-	202	5.2	63	34	17.8	54	138	[42]
Ancona	-	-	-	97.4	18.1	63.9	45.6	50.9	-	199.1	[5]
Torino	-	-	-	149	-	90	191	209	-	183	[100]
Salerno	10.5	304.3	4.1	126	8	75.2	19.4	16.6	56.5	197	[60]
Sopron	-	-	-	109.2	30.8	88.9	-	43.3	-	151.9	[113]
Florida	1.37	36.9	-	39.5	0.71	9.57	16.4	3.55	-	54.6	[114]
European Union (EU)	3.72	-	-	15.3	6.35	13.01	21.72	18.36	-	-	[41]
Turin	11	-	-	124	27	94	233	164	86	170	[99]
Rome	-	-	-	3601.2	-	280.1	-	97.2	-	996.0	[62]
Northern Latium	-	-	18.3	-	-	-	-	-	-	-	[74]

[1] Results obtained in this work.

3.4. Clustering of metals and locations based on similarity

Figure 4 shows the clusters of metals obtained using the Pearson cluster analysis. Overall, six clusters were identified, with cluster one comprising of As; cluster two including Ba, V, and Be; cluster three including Pb and Cu; cluster four comprising of Co; cluster five including Cr and Ni; and cluster six comprising of Zn.

Figure 5 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: "58 Via m. Filippini GG1", "44 Cesano EST VU2", and "Ostia Antica 2 Volponi AC2". Cluster II included four

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locations: "Mariotti 1 Ortaggi AC2", "60 Via Cherasco VU2", "Settebagni 5 AC2", and "Tenuta Columba Salaria 1 AC3". Cluster III included three locations: "Marcigliana 8 AN2", "52 Olgiata NORD VU1", and "49 Via m. Visentini VS2". Cluster IV included one location: "Mongale 3 Prato Naturale IN". Cluster V also included one location: "Ostia Antica 3 Volponi".

The average concentrations of the metals in these five location clusters are shown in Table 5. The table shows that Clusters I and II had lower mean concentrations for most metals, while clusters III, IV, and V had higher mean concentrations for several metals.

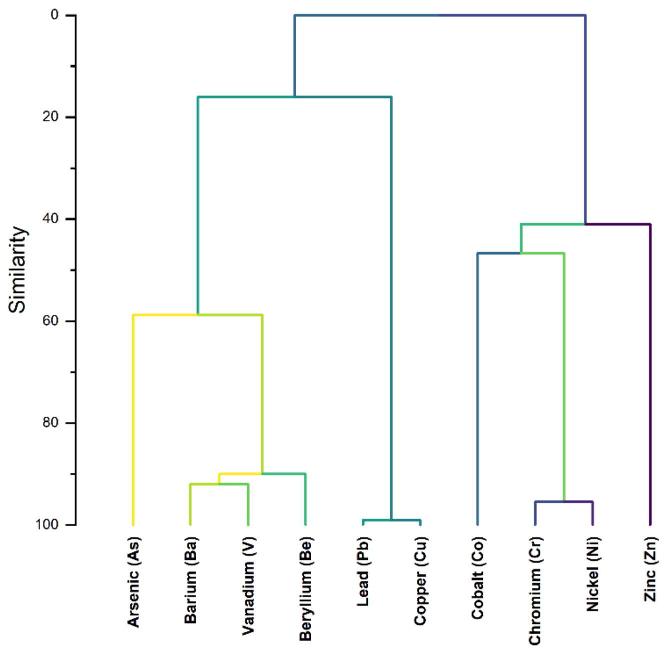

Figure 4. Pearson Cluster Analysis for metals based on similarity.

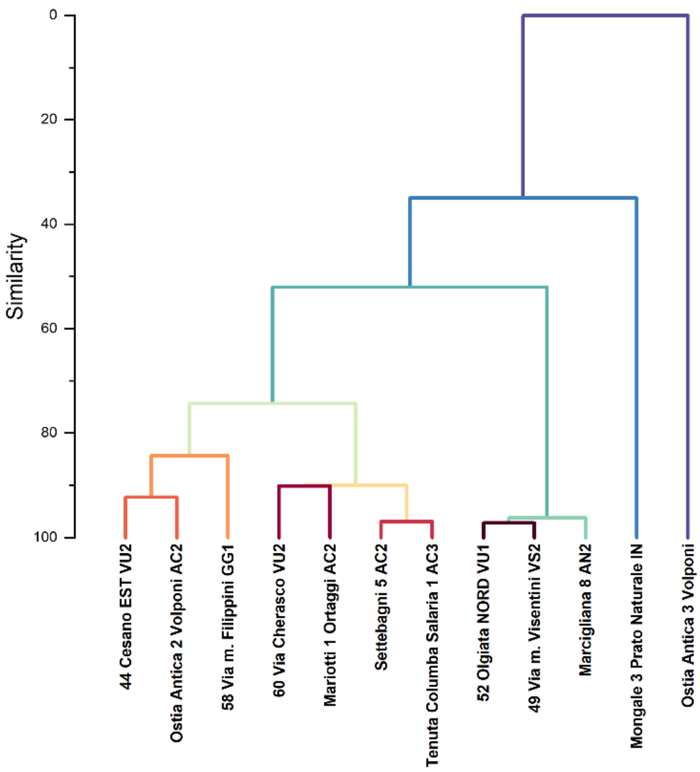

Figure 5. Pearson Euclidean vertical Cluster Analysis with dendrogram showing five groups of clusters based on similarity.

Table 5. 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**

3.5. Principal component analysis to assess the anthropogenic relationship between study locations and metal concentrations

Figure 6 depicts the 3-dimensional principal component analysis (PCA) Biplot for sampling locations and metal concentrations, along with the PC1, PC2, and PC3 components (generated using OriginPro 2021) [94], 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 6 indicates the anthropogenic relationship of two study locations North of Rome (Figure 1) ("49 Via m. Visentini VS2", and "52 Olgiata NORD VU1") with the high concentrations of As, Ba, Be, and V. In addition, it also indicates the anthropogenic relationship of one study location South-West of Rome ("Ostia Antica 3 Volponi") with the high concentrations of Cu, and Pb. Notably, the soils of these three sites are predominantly being used as croplands according to the data from ESA WorldCover 2021 [91].

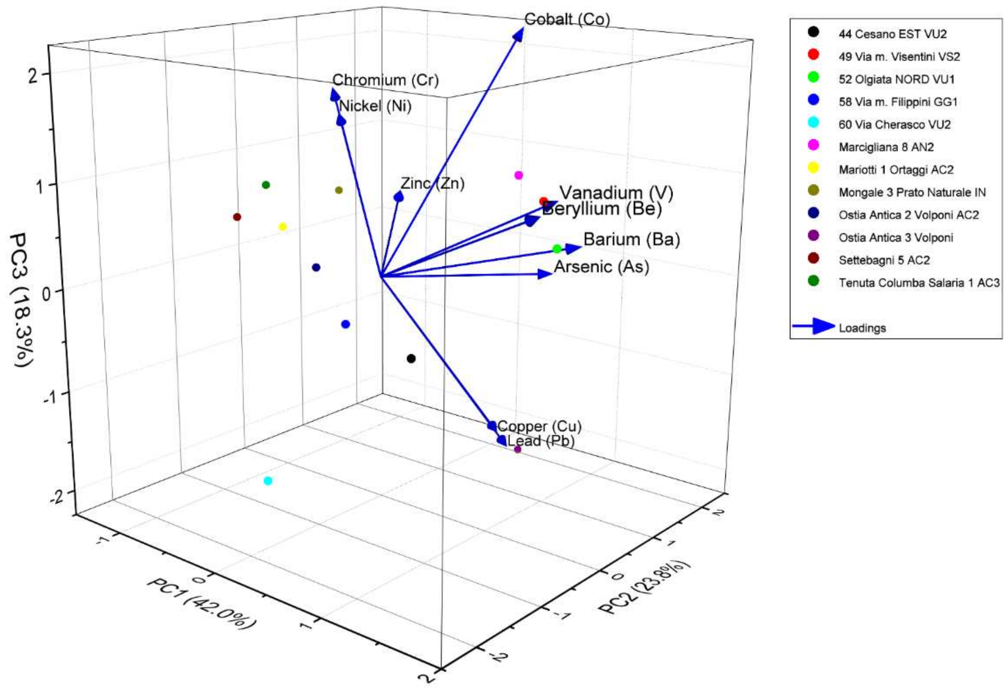

Figure 6. 3-Dimensional Principal Component Analysis (PCA) Biplot for sampling locations and metals showing PC1, PC2 and PC3 components.

Figure 7 depicts the 2-dimensional PCA Biplot for sampling locations and metal concentrations, along with the Dim1 (42%) and Dim2 (23.8%) components (generated using R, version X); thus, the two factors (Dim 1 and Dim2) together accounted for nearly 66% of the variance in this analysis. Moreover, Figure 7 indicates the anthropogenic relationship of three study locations North of Rome

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(Figure 1) ("Marcigliana 8 AN2", "49 Via m. Visentini VS2", and "52 Olgiata NORD VU1") with the high concentrations of As, Ba, Be, and V. This analysis also indicates the anthropogenic relationship of one study location South-West of Rome ("Ostia Antica 3 Volponi") with the high concentrations of Co, Cu, and Pb and that of another study location South-East of Rome ("Mongale 3 Prato Naturale IN") with the high concentrations of Cr, Ni, and Zn.)

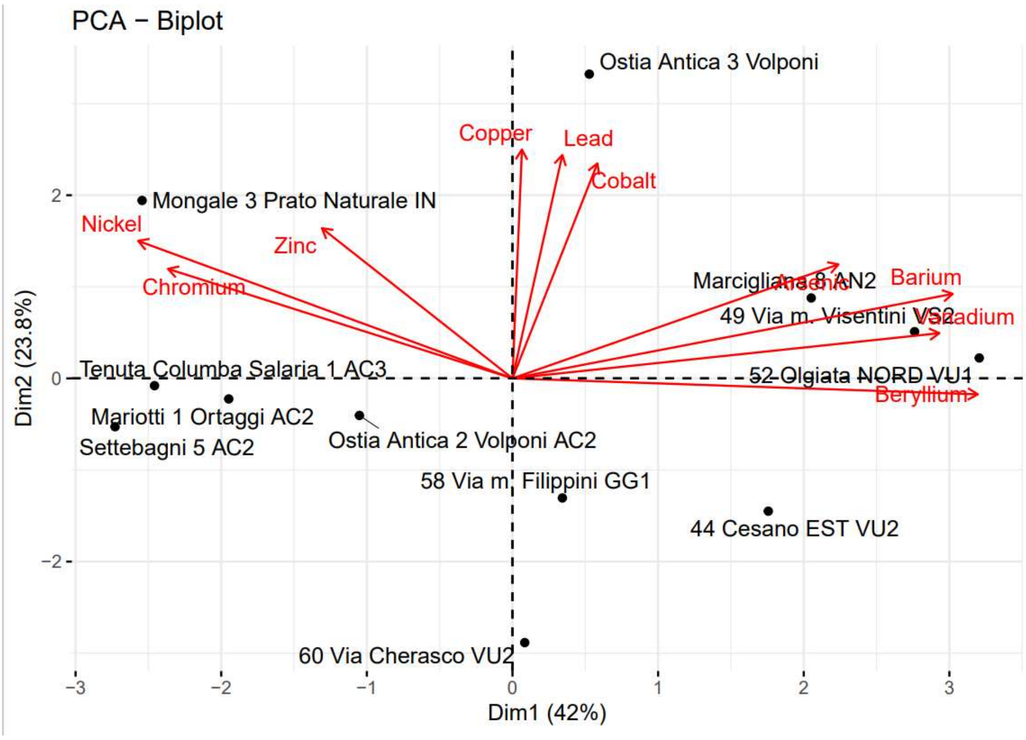

Figure 7. 2-Dimensional Principal Component Analysis (PCA) Biplot for sampling locations and Metal content.

3.6. Correlation matrix of studied metals to assess the anthropogenic relationship between metal concentrations

Figure 8 shows the Pearson correlation coefficient matrix of the studied metals (generated using OriginPro 2021) [94]. In this study, the five most strongly positively correlated pairs of metals 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 metal 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 ($r = -0.46$). Among these correlated pairs, the pair of Cu and Pb can be considered of particularly high interest because of the unusually high concentrations of both these metals in one study location ("Ostia Antica 3 Volponi" with Cu concentration of 310 mg/Kg against the permitted limit of 120 mg/Kg and Pb concentration of 1200 mg/Kg against the permitted limit of 100 mg/Kg).

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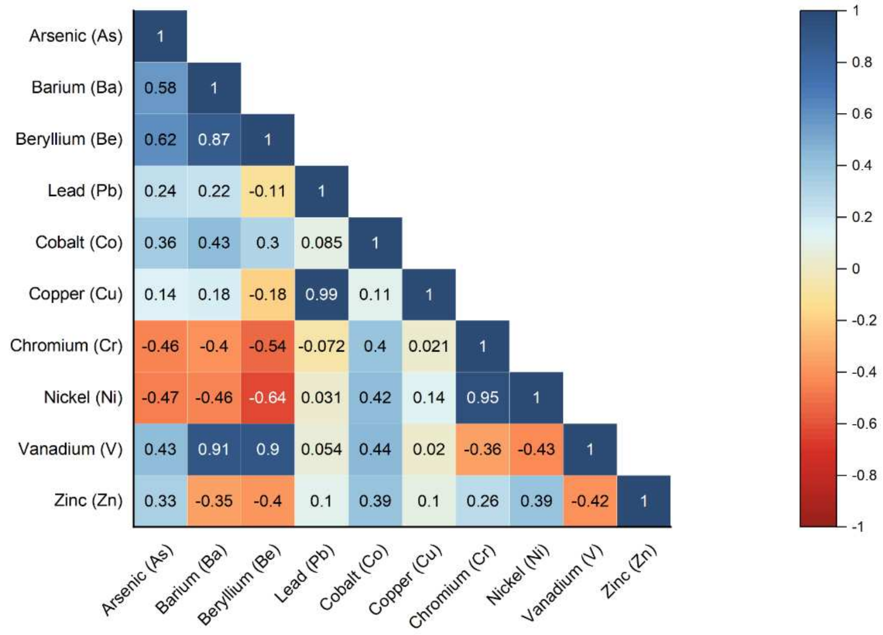

Figure 8. Pearson Correlation Coefficient Matrix for metals under study.

4. Discussion

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

Soils of urban areas can be extensively exposed to metals 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 metal 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 metal that was obtained by adding one-half of the standard deviation to the arithmetic mean for that metal in various study samples. In this study, in addition to the permitted regulatory limit (Limit A) [70], we used the "Q3 value" for the metal concentrations to identify hotspot soils and labelled the locations with metal concentrations beyond the Q3 concentrations as "worthy of scrutiny" (Box 1).

Therefore, among all studied clusters, clusters 3, 4, and 5 contained the most hotspot soils for most of the studied metals. These results suggest that there is a need to reexamine the soil standards for urban soils in the context of high metal concentrations bioavailability, and a systematic approach to defining hotspots is necessary to limit the unwanted pubic health impacts of metal pollution.

4.2. Anthropogenic and Geogenic Contributions to Metal Enrichment of Soil

Whether these hotspot soils with unusually high metal concentrations are anthropogenic or geogenic (volcanic) can be debated because of the mixed results of earlier studies [115] and considering the origin of Roman soils from volcanic rocks [28]. Volcanic soils can be naturally expected to contain a relatively higher concentration of metals than non-volcanic soils [116]. However, the results from various analyses used in this study also support an important anthropogenic contribution to the high metal concentrations found in most of the hotspots in this study. First, during the descriptive analysis for metal 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 3-dimensional PCA,

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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 2-dimensional PCA showed consistent results with the 3-dimensional PCA. Fourth, in the Pearson correlational matrix analysis, several pairs of metals 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 metals.

Box 1: Study locations worthy of scrutiny for evaluated metals.

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.

Taken together, these analyses indicate that anthropogenic factors are closely involved in the high concentrations of metals in this study. Several prior studies have also used these analyses to confirm the anthropogenic causes of high metal concentrations in the soils [52,54,105]. A study from Rome by Calace et al. [62] 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 metal concentrations. For instance, in southern Italy (Solofrana river valley), a study has found high concentrations of Cr and Cu in agricultural soils [63]. Another study from Torino, Italy, found high concentrations of Cu, Pb, and Zn within the city's soils [100]. In general, the metal concentrations reported in the present study were largely consistent with the previous studies from Italy [5,95,100].

The results of the present study were also compared with those from Europe, the United States, Asia, and Africa (Table 3). In general, the metal 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 metal 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 though the presence of volcanic soils makes Italy's soils richer in metals 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 metals (Cu, Pb, Zn, etc.) which manifests as unusual clustering of those metals in certain locations.

5. Conclusions

The multifunctional urban agriculture initiatives in Rome, particularly those undertaken by young farmers through 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 [85].

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 [117].

Indeed the introduction of urban gardens, 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 cities sustainability. However, as 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 into 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, contribute to relatively high levels of barium, beryllium, arsenic and vanadium, and taking into consideration the great toxicity of some of these metals the human health risks of using these soils as urban gardens 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.

In conclusion, this study collectively underscore 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 heavy metal 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 through the food chain emphasize 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 "Settebagni 5 AC2" met the limit A concerning all the metals analyzed. The soil from Ostia Antica 3 Volponi was found unsuitable for agriculture purposes because it had 1200 mg/Kg of Pb. Moreover, several locations were found to have very high concentrations that are worthy of scrutiny and detailed studies. Though the results of this study are limited by a small number of study locations and samples, these results indicate that high metal 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 metals on agricultural output and public health.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Figure S1: Map showing spatial distribution of metal content with the Land Use Land Cover (LULC) from ESA WorldCover 2021 at the background.

Author Contributions: Conceptualization, reconstruction of CTR mosaic, georeferencing and digitization of soil map of Rome, Italy-M.S.C., I.M.S., and J.E.S.; writing—original draft preparation, M.S.C., I.M.S. and J.E.S.; writing—review and editing, M.S.C., I.M.S. and J.E.S.; supervision, I.M.S. and J.E.S.; funding acquisition, I.M.S. and J.E.S.; Soil collection - S.M and R.M. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflict of interest.

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