JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2024, 25(5), 335–350
https://doi.org/10.12911/22998993/186662
ISSN 2299–8993, License CC-BY 4.0

Received: 2024.03.12
Accepted: 2024.03.26
Published: 2024.04.02

Potentially Toxic Elements in Urban and Peri-Urban Soils – A Critical Meta-Analysis of their Sources, Availability, Interactions, and Spatial Distribution

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ABSTRACT

The current study attempted to incorporate the major aspects of heavy metal pollution in urban and peri-urban soils. Urban soils are a type of currently problematic soil that accumulates a great quantity and diversity of pollutants, a high population load, and a wide range of activities within a very limited area. From 2010 to the present, published studies in the Scopus database on urban soil contamination in various places across the world were studied, evaluated, and discussed. The pollutant levels were statistically processed, and new data were obtained as a consequence of a meta-analysis of the soil contamination and ecological risk indices of the research locations. The soil environment links plants, animals, and humans, as well as living creatures and inanimate substances transported to water and to the air environment. Activities in the soil have as a final destination groundwater, recycling, and reproducing pollutants and chemicals, with heavy metals or potential toxic elements as the major actors. Soil-based urban pollution is of particular concern in soil science as it may be a rising risk for the environment and humanity in the near future.

Keywords: urban soils; soil pollution; heavy metals; potentially toxic elements.

URBAN AND PERI-URBAN SOILS DEFINITION

Urban soils occupy only 3% of the earth's terrestrial surface (Li et al., 2018). These areas concentrate more than 50% of the human population, with estimates indicating that this is projected to increase to 66% by 2050 (United Nations, 2014). As a term, "urban soils" was first introduced in the early 1960s to describe the characteristics of disturbed soils in urban areas and raise the awareness about potential risks (Dutta et al., 2022). Since 2000, several researchers started using a broader term, "anthropogenic soils", to include natural soils which although they were far from urban areas, were indirectly facing the consequences of human activities (Pouyat et al., 2020). Urban soils are formed either after prolonged human intervention or due to sudden and intense concentration of human activity in a certain location and in a given environmental background (Aslanidis & Golia, 2022; Papadimou et al., 2023). Unlike natural or agricultural soils, urban soils are influenced both by the local microclimate and the formation process, as they retain characteristics from the parent rock that affect their physicochemical properties and nutrient cycles (Golia et al., 2021b). Furthermore, they frequently have irregular layering, fragile structures, and high amounts of trace elements (Ajmone-Marsan & Biasioli 2010). Peri-urban soils are a vital component of the urban areas, providing essential ecosystem services such as food production, water filtration, and carbon sequestration. However, increasing urbanization and industrialization also have a significant impact on them (Chen et al., 2020). These soils are particularly vulnerable to degradation by heavy metals (HM) or other pollutants due to human activities such as agriculture, waste disposal, and transportation (Golia et al., 2021a). Urban expansion into peri-urban zones has also contributed to soil erosion, and loss of biodiversity, compromising soil's ability to support food production and other ecosystem services (Mukherjee et al., 2016).

HEAVY METALS AND POTENTIALLY TOXIC ELEMENTS IN URBAN AREAS

HM and metalloids are a group of elements with density greater than 5 g/cm³ and pose significant threat to human and environmental health (Kiris & Baltas, 2021). Such metals and metalloids are mercury (Hg), zinc (Zn), cadmium (Cd), nickel (Ni), arsenic (As), chromium (Cr), copper (Cu), and lead (Pb). These elements accumulate in all living organisms and are extremely toxic in high concentrations. Their toxicity depends on their chemical characteristics, concentration, and path of exposure (ATSDR, 2015). Potentially Toxic Elements (PTEs) is a term frequently used by scientists to emphasize these elements' negative effects on organisms when their concentration exceeds specific limits (Bourliva et al., 2021). HM concentration in urban and peri-urban topsoils is a significant indicator of environmental pollution since they persist unmodified in soils for several years (Massas et al., 2018). Their decomposition is impossible, except for when they change chemical form (organic or inorganic) under specific and strict conditions (Silva et al., 2021; Golia, 2023). Such occasions are their combination with oxygen to form oxides or with dead organic matter (Bradl et al., 2005; Golia et al., 2023). Research on HM pollution in urban areas has increased recently due to the potential hazards for public health. He et al. (2023) studied the distribution of metals in topsoil and dust in China, as these are strong indicators of simultaneous metal concentration interference. A similar study was conducted by Li et al. (2022). Both researchers found that dust was more contaminated than soil in urban areas. Pb, Zn, and Cu were more common in both soils and dust, while greater amounts of Hg and As were found in highly industrialized areas. Kelepertzis et al. (2020) studied anthropogenic contamination in urban soils using Pb isotopic ratios. They found that human influence in terms of metal (loid) concentrations was more pronounced for the road and house dust material as the Pb soil isotopic ratios were higher than 1 (206Pb/207Pb = 1.154 to 1.194). Argyraki et al. (2018) investigated the environmental availability of common elements, in urban, peri-urban, rural soils, and mining areas of Greece, highlighting the parameters that differentiate and control metal mobility. Petrik et al. (2018) used data from Campanian topsoil to perform compositional discrimination analysis and explore the source patterns of Zn, Pb, Cr, and Ni. Due to extensive traffic and alloy production, the massive urban and industrial regions were primarily contaminated with Pb and Zn. In another basin, highly polluted from tannery waste, increased amounts of Cr and Ni were found. The researchers also noted that the geogenic abundance of Zn and Pb is a common feature of the big volcanic complexes, while siliciclastic deposits are mostly linked to the Cr and Ni geogenic richness.

SOURCES OF URBAN SOILS' POLLUTION

Urbanization and industrialization that have grown rapidly, together with high population density, have led to excessive consumption of natural resources. Intensive human activities produce large quantities of organic and inorganic waste, including HM (Papadopoulou et al., 2014; Sparks et al., 2023). Statistical methods are frequently used to find the possible sources of soil pollutants. Guillén et al. (2012) used HM fractionation and multivariate statistical techniques to evaluate the environmental risk in soils. According to their results, household and industrial activities, transportation, and coal burning emissions were the main sources of large amounts of HM deposits. Furthermore, Rouhani et al. (2023) found that roadside soils in Pakistan were primarily contaminated with Ni, Zn, Cd, and Pb. The proximity of highways appears to impact HM distribution, as their concentration was found to decrease with distance. According to Shen et al. (2022), the primary contributors to HM accumulation in urban surface soils in China are natural processes, manufacturing activities, agricultural operations, and traffic emissions. As noted by He et al. (2023), HM levels in urban and peri-urban soils vary widely due to diverse local factors such as the location and intensity of pollution sources. Due to the high number and density of emission sources in cities, HM soil concentrations typically decrease along the urban and rural gradients. Serrani et al. (2022) concluded that activities related to metal mining or processing, the use of fossil fuels for heating, traffic, liquid and solid waste, and the excessive use of fertilizers and pesticides are the main sources of urban soils' HM pollution. In Tuscany, Petrini et al. (2022) identified metallurgical activity as the primary source of PTEs detected in soil and groundwater. Kalyvas et al. (2018) noted that topsoil pollution could be an ecological footprint of historical mining activities in Greece. Significant amounts of HM end up in urban and peri-urban soils through aerial deposition (Jayasire et al., 2014). Several studies have shown that aerial deposition is spatially focused as metal levels decrease with increasing distance from the pollution source, while it only affects the surface in the form of soil and road dust (Roy et al., 2023). Industrial and urban emissions due to fossil fuels burn have been found to be responsible for high Pb levels in urban soils (Guagliardi et al., 2015). The presence of As has been linked to emissions from peri-urban industrial and agricultural areas and mining activities. Cd, another toxic element, is primarily released from industrial activities such as battery production and smelting (USEPA, 2000). Metal plating, leather tanning, and textile dyeing have the potential to release Cr, while waste incineration and coal combustion are main sources of Hg emissions (USEPA, 2013). Although industrial companies make significant contributions, traffic emissions remain among the leading causes of HM pollution, especially in cities with limited industrial activity (Silva et al., 2021; Li et al., 2022). Vehicle fuels have been the primary contributor to Pb emissions. At present, even though Pb additives have been eliminated from fuels, Pb can still be detected in urban soils. In addition, car brakes and tire wear are the main sources of Cr and Ni emissions. These two elements, also have a close connection to the parent material. This trend has been identified in several studies (Golia et al. 2021b; Papadimou et al. 2023).

HEAVY METALS' SPATIAL AND SEASONAL VARIATION IN URBAN SOILS

Gong et al. (2010), in China, studied the potential of assessing the HM contamination and the pollution sources using a GIS-based approach and multivariate analysis of urban and rural surface soils. Díaz Rizo et al. (2013) studied in Cuba the spatial distribution of HM in urban topsoils. Higher amounts of Ni were detected in overpopulated areas. Zn and Pb were found in urban green spaces and residential areas. Spatial distribution of Cr, Co, Ni, Pb and Zn followed a similar pattern. However, Cu distribution was significantly different. Benhaddya and Hadjel (2014) investigated the spatial distribution and the degradation levels of HM in topsoils of Algeria. Higher levels of Cu, Mn, Pb and Zn were detected while, Ni concentration was equivalent to background. The highest HM levels were found in industrial areas, in contrast to the rural ones. Mihailović et al. (2015) used a GIS based approach to study HM spatial distribution in urban soils of Serbia. Ordóñez et al. (2015) explored the spatial and temporal variation of trace elements in urban soils and street dust in a highly contaminated Spanish city. Soleymani et al. (2022) investigated HM seasonal variation in urban soils of Iran, including high, low traffic areas, and rural areas, during summer and winter. Tsamos et al. (2022) studied the distribution along with the temporal variability of uranium (U) and various metals (Cu, Cd, As, Cr, Fe, Mn, Ni, Pb, Zn) in snow and rainwater near an oil industry in Greece. They found high pollutants levels that contribute to soil emissions. Papadimou et al. (2023) in Greece used GIS to depict HM pollution and variability over 5 years' time and construct thematic maps for soil pollution indices. Polyakov et al. (2021) in a study conducted in Russia found that HM spatial distribution was highly influenced by anthropogenic activities. Liu et al. (2020) constructed an HM spatial distribution map based on a theoretical model and the corresponding semi-barogram parameters using Kriging interpolation. Mehr et al. (2017) explored HM distribution and pollution sources in urban regions of Iran. They discovered that Co, Cr and Ni levels were normal however, As, Cd, Cu and Zn concentration was significantly higher. Stafilov et al. (2022) assessed both natural and anthropogenic factors contributing to the distribution of HM in urban soils of North Macedonia. Specified factors were assessed through factor analysis implementation and distribution maps were created by Kriging interpolation to depict the analyzed components and factors' spatial distribution.

ECOLOGICAL INDICES OF SOIL POLLUTION

Over the last decades the necessity to monitor and evaluate HM, both in rural and urban soils has emerged. Scientists have developed various methods and indices to quantify HM ecological risk assessment (Rouhani et al., 2023). Frequently used indices include Geo-Accumulation Index (I*geo*), Comprehensive Ecological Risk Index (RI), Single Pollution Index (Pi), and Ecological Risks Index for Individual HMs (Ei). Baran and Kiral (2023) used Igeo, enrichment factor (EF) and pollution index (PI) to determine pollution levels in urban soil samples. Silva et al. (2021) used EF, Igeo, Contamination factor (Cf) and Pollution Load Index (PLI) to monitor soil pollution in Lisbon. Jamal et al. (2018) used Cf, PLI and Igeo to explore Pb and Zn soil distribution around a smelting plant in Iran. Several more studies have utilized these indicators to assess soil pollution. Roje et al. (2018) detected that trace element concentrations in green parks of Croatia's capital were much higher than the permitted limits. In China, Guo et al. (2012) investigated HM spatial distribution to evaluate urban soil pollution. According to their results, peri-urban and urban industrial areas exhibited the highest concentrations of As, Pb, Zn, and Cu, while lower levels were detected in urban parks. Karim et al. (2015) determined HM geochemical baseline in urban soils of Pakistan, using ecological indicators as a useful monitoring tool. Similarly, Urrutia-Goyes et al. (2017) explored Ni, Zn and Pb contamination in the subsoil of a historic firing range restored in an urban park, concluding that such parks contribute significantly to soil contamination. Massas et al. (2010; 2013), calculated HM availability indicators in playgrounds in Greece. Availability proportions were determined, and their distribution was displayed over the entire city footprint using the GIS software. It was found that recent HM contamination incidents had primarily affected playgrounds in the municipality's southern and eastern regions. Pietrelli et al. (2022) studied HM bioaccumulation in urban grass and compared it with data from rural areas. They found that HM soil concentration was higher for Zn but significantly lower for Cr and Cd.

SOIL POLLUTION DETERMINING FACTORS

HM and PTE enrichment of urban soils poses a significant threat to their long-term viability, as well as to residents' living and working conditions (Luo et al., 2012; Argyraki & Kelepertzis, 2014). Lu and Bai (2010) investigated HM contamination and mobility in urban soils of Hangzhou, China. They found a strong relationship between land uses and HM concentration. Furthermore, Xia et al. (2011) concluded that land use is a key parameter in HM pollution determination in topsoils. Serrani et al. (2022) highlighted that in urban soils of Italy a higher HM spatial variability was detected compared to agricultural or natural areas, as these soils are often mixed with extraneous materials. To effectively assess HM impact on soil functions, the researchers recommended using HM available, rather than pseudo-total or total concentration. Mihailović et al. (2015), in a study conducted in Serbia, found that Cu, Pb and Zn originated primarily from anthropogenic inputs, while As, Co, Cr, Mn and Ni had a natural origin, as confirmed by correlation matrix and multivariate statistical analysis. Yang et al. (2011) investigated HM potential sources of contamination in urban topsoils of China. According to their results, high amounts of Zn, Cd, Pb, Hg and Cu were detected. Correlation coefficient analysis revealed that highly toxic elements such as As, Hg and Cd were significantly positively correlated with each other, isolating Cr and Mn in a separate group. Furthermore, traffic was found to be the major source of HM urban pollution. Numerous studies indicate that PTEs both distribution and levels affect soils' physicochemical properties. Cai et al. (2013) investigated HM contamination in urban soils and dust in China. By using multivariate statistical analysis, they found that Cr and Ni detected were mainly of natural origin, while Cd, Cu, Pb, and Zn were derived from anthropogenic activities. Bedrock and the geochemical composition of substrate appear to define HM distribution (Guagliardi et al., 2012). However, Zn, Pb and Cu concentrations are further influenced by land uses and human-induced pollution in urban areas. Hoshyari et al. (2023) demonstrated that land uses influence both the spatial distribution and the ecological risk of PTEs, Rare Earth Elements (REEs), and nutrients. Kourgia et al. (2022) explored the fate of trace elements in sediments following a major flood event in Greece resulting in serious soil pollution. According to Botsou et al. (2022) both organic carbon and $CaCO_3$ can be assessed to determine the HM content extracted from soils. Significant amounts of PTEs seem to accumulate mainly in the residual fraction, showing that this fraction is a valuable indicator of anthropogenic urban pollution. The effect of land uses on HM soil accumulation was also investigated in Turkey by Vural et al. (2021). Foti et al. (2017) investigated PTEs levels and soils' degradation in urban areas and parks of France. Weber et al. (2021) conducted an important study on HM spatial variability in pavement joints in Germany. Significant amounts of PTEs detected appear to present high risk for urban ecosystems. To create efficient management methods for urban soil pollution, it is necessary to consider runoff-related transportation procedures, as well as urban geochemical background values. Furthermore, microclimate can regulate several soil parameters, affecting metals mobility and availability in urban soils (Said et al., 2019). Different land uses together with regional landscape appear to determine metals availability (Guven, 2019).

SOIL SAMPLING AND ANALYTICAL METHODS FOR HEAVY METAL DETERMINATION IN URBAN AREAS

After reviewing several studies on urban soil pollution, it was established that there is no standard technique for soil sampling in urban environments. Johnson and Demetriades (2011) highlighted that sampling depth varies considerably, ranging between 0-25 cm, depending on the research purpose. Sampling techniques and design vary significantly. Composite soil samples from different (4-6) sites are frequently used. However, sampling from a single site or point samples is also a common practice. Composite samples are used to estimate the average value of both physicochemical parameters and PTEs contained in the soil, while point samples reflect the geochemical content of the area in question. Determination is usually based on the potential heterogeneity within the study area, especially in highly populated urban environments. The least disturbed area of an open space is selected to ensure the least possible variability. Before soil sampling, foreign substances such as debris or stones are removed from the area of interest. Soil sampling design may be either random or systematic using a grid. Sufficient number of samples should be collected from urban areas to identify, with a high level of confidence, both local background and outlying or limiting samples. Tresch et al. (2018) in Switzerland evaluated 37 urban soil quality indices obtaining more than 150 soil samples from urban green spaces and gardens. Furthermore, Świdwa-Urbańska and Batlle-Sales (2021) obtained numerous soil samples in their study to ensure high data quality and provide representative results to soil scientists and decision makers. Kelepertzis and Argyraki (2015) separated the soils' fractions to carry out metal quantification. Inductively coupled plasma - mass spectrometry (ICP-MS) and Aqua Regia digestion were used to determine Hg levels in the soil fraction below 100 μm. Silva et al. (2021) determined PTEs concentration using Atomic Absorption Spectrophotometers with Graphite Furnace GF95 equipment, in a Thermo Elemental SOLAAR, Suite M5 Spectrometer, with an automatic sampler FS95, controlled by SOLAAR software, v.11.2. Keramari et al. (2023) presented an innovative perspective involving PTEs ions electroanalysis in their study on toxic (Cd, Pb) and trace elements (Cu, Zn). The methods described refer to the development and application of new electrode surfaces, are rapid and economical, allowing the simultaneous determination of all metallic elements in the extraction solution from urban soil samples.

METHODOLOGY OF THE STUDY

The present study comprises of a literature review on urban and peri-urban soils' HM pollution followed by a data meta-analysis. Primary goals were to: 1. Investigate and highlight the parameters regulating urban pollution, 2. Explore the correlation between HM and PTEs levels in urban soils, 3. Highlight their potential sources of origin to serve as a legacy and precursor for future research and raise awareness of both stakeholders and policymakers. In depth research of relevant scientific studies from 2010 onwards was conducted in the Scopus database. The keywords used were heavy metals, urban soil, and pollution. Obtained data were statistically processed. Correlation method was performed at 95 and 99% significance level. Principal Component Analysis was also performed and the groups of metallic elements that had a common origin were presented. Therefore, a data meta-analysis was performed, and new evidence and conclusions emerged. In addition, XLStat software was used for the graphical representation of the results.

POTENTIALLY TOXIC ELEMENTS STUDIES PER COUNTRY

Figure 1 presents the number of conducted studies for each metal, per country. A significant number of publications were observed in China.

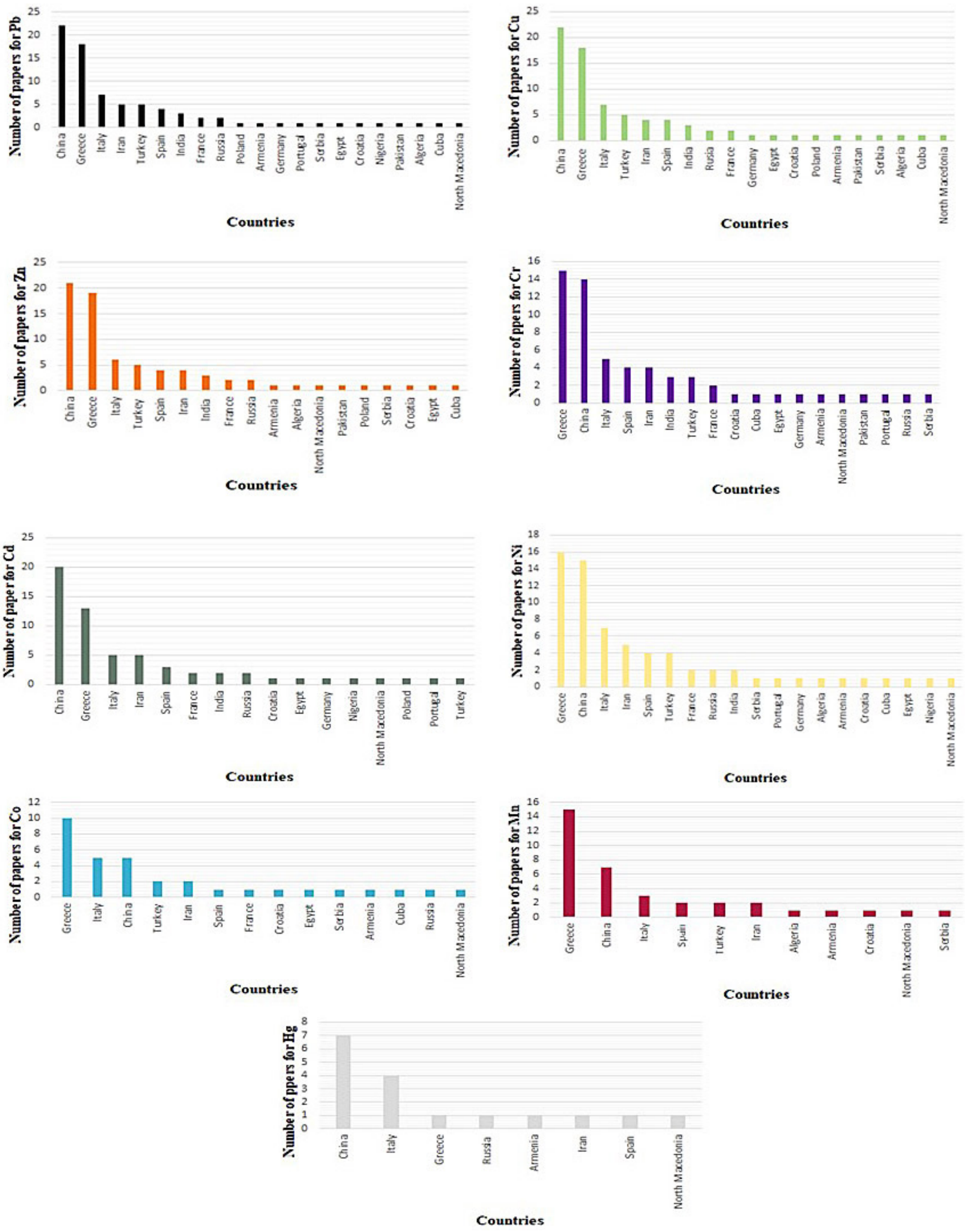

Figure 1. Number of studies per metal and per country

Furthermore, several studies have been implemented in the Mediterranean region (Greece, Italy, and Turkey) about HM pollution in urban and peri-urban soils. In terms of Pb-related publications, China ranks first in the number of publications, followed by Greece and Italy, which follows in third position with a significant gap. Pb is the most studied HM globally. Likewise, China is the country most frequently publishing studies regarding Cu, Zn and Cd. Greece is in second spot, while Italy comes third. Greece had the most publications about Cr, Ni, Co and Mn, while China and Italy for Co. Although Hg is of major environmental interest, it is often not detectable in urban soil samples, and it is the least studied HM globally. The most studies about Hg have been conducted in China while, Italy and Greece are second and third respectively.

HEAVY METALS AND POTETIALLY TOXIC ELEMENTS CONCENTRATION IN URBAN SOILS

According to the literature review many authors support that high HM and PTEs pollution load in urban soils is mainly due to human activity (Kannan et al., 2023; Qiao et al., 2023). Furthermore, traffic and industrial emissions are the primary sources of Cd, Cu, Pb, Zn, Cr, and Ni in urban soils (Li et al., 2023; Rouhani et al., 2023). Soleymani et al. (2022), reported that in urban areas with heavy traffic, HM levels are higher than those with lower traffic. Still, other studies state that in addition to the pollution of urban soils from the road network, the impact of municipal construction facilities is also significant. There is an urgent need of mitigation since the construction materials and their transportation enhance urban soils' HM pollution (Li et al., 2022; Kosheleva et al., 2018). More specifically, other studies emphasize that vehicle exhaust emissions, coal gangue, flying ash and industrial wastewaters are the primary sources of Cu, Cr, Cd and Pb, while the main source of Hg and As is the coal combustion (Ying et al., 2016; Ma et al., 2016). Urban areas with higher levels of urbanization have a higher accumulation risk of Cd, Cu, Pb and Zn. Other influencing factors such as land use, urban environment, and wind speed have a less pronounced contribution (Liu et al., 2016). Qiao et al. (2023) in China observed that there is a variety in HM concentration and distribution in the capital's urban soils. Furthermore, layered structure may result from a variety of sources with varying degrees of influence. Akinsete and Olatimehin (2023) found that there is a significant increase in health risks when heavy metals are combined with organic pollutants such as PAHs in urban roadside soils in Nigeria. Table 1 presents HM and PTEs minimum and maximum concentrations per country, and Table 2 presents the mean concentrations and the standard deviation per metal and per country.

For Pb most countries seem to be below 100 $mg \cdot kg^{-1}$, however significantly increased mean values are found in Portugal and Spain. In contrast, the lowest average concentration is observed in France. Urban soil contamination from Pb is a serious environmental problem having detrimental effects on both human health and ecological ecosystems (Silva et al., 2021). Due to the excessive use of Pb based paints, industrial and traffic emissions, urban areas are particularly vulnerable

Table 1. HM and PTEs concentration range per country

Country	Pb	Cu	Zn	Cr	Cd	Hg	Ni	Co	Mn
	$mg \cdot kg^{-1}$ dry soil								
China	7.3–275	1.5–189.9	52.4–373	22.4–228	0.13–3.74	0.04–3.30	11–63	7.9–20.1	374.5–743
Greece	561–2.45	215–11.7	271–47.45	438.29 –3.63	2.60–0.17	0.87	327.46–3.62	34.9–1.04	1985–5.97
Italy	247–24.21	145–20.81	233–90	95–7	1.38–0.40	166–0.21	60–10	18.10–8	864–555
Iran	275.90–36.33	732.90 74.86	470.36–88.7	105.5–46.97	2.17–0.35	0.12	108.41–20	14.60–13.15	622–430.01
Turkey	191–38	68.7–34.42	255–52	125–14	0.21	–	99–15	17.7–5.40	475–284.10
Spain	550–35.4	56.35–18.68	1259–2.41	40–15	17.20–0.21	0.15	49–5	13.06	1342–458
India	79–73.85	69.18–32.48	437–59	412.28–58.91	5.5–1.1	–	371–20	–	–
France	35.24–22.9	68.60–39.30	140.89–117	30–14.22	1.44–0.68	–	20.92–14.23	6.88	–
Russia	116.76–65.4	92.45–41.6	207–90	98	2–0.4	0.12	27–18	7.20	–
Poland	77	13.17	99.17	–	0.79	–	–	–	–
Armenia	42.50	86.87	262	122.00	–	0.63	61.90	13.70	776
Germany	68.60	19.39	–	157.10	1.20	–	160.20	–	–
Portugal	130.97	–	–	44.00	0.46	–	46.60	–	–
Serbia	42.00	94	100.30	28.00	–	–	28.70	7.30	368.60
Egypt	30.20	26.58	210.40	32.60	0.90	–	77.10	286.80	–
Croatia	61.40	27.50	178	72.20	0.41	–	39.60	21.00	85.20
Nigeria	45.10	–	–	–	2.80	–	24.30	–	–
Pakistan	82.30	48.00	99.52	9.31	–	–	–	–	–
Algeria	33.43	60.11	61.08	–	–	–	35.78	–	121.21
Cuba	68	17.40	199	97	–	–	35	14	–
North Macedonia	41.50	38.80	86	74	0.43	0.19	62	28	670

Table 2. HM and PTEs mean concentration per country

Country	Pb	Cu	Zn	Cr	Cd	Hg	Ni	Co	Mn
China	50.97±1.2	44.51±1.5	143.78±5.7	70.84±2.2	0.63±0.7	0.60±0.04	31.00±2.9	15.00±0.9	570.89±11.2
Greece	87.72±3.3	75.70±2.5	118.08±2.9	117.61±6.2	0.69±0.3	0.87±0.01	92.64±2.7	19.20±0.5	602.89±12.9
Italy	113.37±4.7	53.71±1.1	156.00±1.7	51.00±1.4	0.82±0.4	41.98±2.1	33.00±0.9	13.00±0.9	701.00±11.7
Iran	113.17±3.9	250.87±9.2	246.00±6.9	74.46±1.4	1.52±0.5	0.12±0.01	61.22±2.4	13.88±2.1	526.01±15.8
Turkey	93.39±2.1	46.67±1.3	113.00±7.3	55.00±0.7	0.21±0.1	-	49.00±1.9	11.55±1.5	380.00±11.6
Spain	177.57±7.2	37.19±1.1	496.00±8.8	31.00±0.9	7.49±1.1	0.15±0.3	24.00±1.3	13.06±1.6	900.00±19.2
India	76.51±4.5	54.22±1.9	198.41±3.2	238.43±6.3	3.30±0.2	-	195.00±4.7	-	-
France	29.07±1.7	53.95±1.1	129.00±2.4	22.00±0.1	1.06±0.6	-	17.58±1.6	6.88±1.3	-
Russia	91.08±2.4	67.02±1.5	199.00±3.3	98.00±5.2	1.10±0.5	0.12±0.02	22.00±2.2	7.20±0.8	-
Poland	77.00±1.6	13.17±0.8	99.17±1.5	0.00	0.79±0.4	-	-	-	-
Armenia	42.50±0.9	86.87±1.5	262.00±7.2	122.00±9.9	-	0.63±0.02	61.90±4.2	13.70±1.6	776.00±11.8
Germany	68.60±3.8	19.39±0.2	-	157.10±7.2	1.20±0.6	-	160.20±10.2	-	-
Portugal	130.97±8.9	-	-	44.00±3.5	0.46±0.2	-	46.60±2.8	-	-
Serbia	42.00±1.1	94.00±4.2	100.30±1.6	28.00±1.1	-	-	28.70±1.8	7.30±1.1	368.60±12.2
Egypt	30.20±0.9	26.58±1.1	210.40±3.3	32.60±0.7	0.90±0.5	-	77.10±4.8	286.80±6.6	-
Croatia	61.40±1.4	27.50±1.7	178.00±2.7	72.20±3.3	0.41±0.4	-	39.60±2.9	21.00±0.8	85.20±1.9
Nigeria	45.10±0.9	-	-	-	2.80±0.1	-	24.30±1.1	-	-
Pakistan	82.30±3.7	48.00±2.6	99.52±2.2	9.31±0.2	-	-	-	-	-
Algeria	33.43±0.6	60.11±3.2	61.08±3.1	-	-	-	35.78±3.3	-	121.21±12.2
Cuba	68.00±2.3	17.40±0.4	199.00±3.3	97.00±8.2	-	-	35.00±2.8	14.00±1.1	-
North Macedonia	41.50±1.9	38.80±0.6	86.00±2.1	74.00±7.9	0.43±0.2	0.19±0.02	62.00±4.4	28.00±1.7	670.00±21.7

to Pb contamination (Tepanosyan et al., 2017). Numerous studies have demonstrated that Pb contamination is mainly localized, with higher concentrations close to the pollution sources such as industrial sites and highways (Rouhani et al., 2023; Kannan. et al., 2023; Chen and Lu, 2018). Cu in Iran has the highest average concentration value compared to the other countries, with Serbia coming second. It is observed that Mediterranean countries such as Greece, Italy, Spain, Turkey and France seem to have similar variation in Cu concentration values in their urban soils. Urban soils frequently include Cu contamination, which is mostly caused by human activity and industrial operations. Cu pollution is more likely to occur in urban locations where there are extensive industrial operations, wastewater discharges and agriculture practices. Levels of Cu in urban soils are additionally influenced by plumbing materials, electrical wiring, wood preservatives and fungicides (Chen et al., 2016). In this study literature review showed that urban areas that were close to pollution sources like roads, industrial sites, and regions close to agriculture activities had higher concentrations of Cu contamination in urban soil (Shen et al., 2022). Regarding Zn, Spain has the highest average concentration value, followed by Armenia. Algeria and North Macedonia shows the lowest average Zn concentration. Urban soil pollution with Zn is a common issue mainly caused by anthropogenic activities and industrial processes. Urban areas with mining, smelting, and manufacturing facilities, are exposed to Zn contamination (Li et al., 2013). Furthermore, the use of Zn containing products and atmospheric depositions from various sources have a significant impact on soils' pollution. In urban areas Zn contamination tends to be higher near places such as industrial zones and motorways (Ma et al., 2016). For Cr, India has by far the highest average concentration value as well as the largest range of values compared to the other countries. Among the Mediterranean countries, Greece has the largest range of values and the second highest average concentration value of Cr after India. Other Mediterranean countries such as Italy, Turkey, France, and Spain show similar variation. Qiao et al. (2023) in China revealed that Cr levels were higher in peri-urban areas. For Cd almost all countries show similar variation in their mean concentration with values below 2 mg kg^{-1} with the only exception being Spain with the highest mean concentration and the broadest range of values, followed by India and Iran. The contamination of urban soils from Cd is primarily a result from industrial activities, the use of phosphate fertilizers and the spread of sewage sludge (Liu et al., 2020). Cd pollution is more likely to occur in urban areas with industries such as metal plating, battery manufactures and wastewater treatment facilities (Liu et al., 2020). Contamination of urban soils with Cd tends to be localized because it is typically higher near the pollution sources (Qing et al., 2015). For Ni, the highest average concentration is found in India, followed by Germany. Italy, France, Spain, Turkey, Croatia and Algeria seem to follow a similar variation in their mean concentration values for this Cd as well, which is below 50 mg·kg^{-1}, with exception of Greece, which has the highest mean concentration and widest range of values in the Mediterranean region followed by Egypt. Zheng et al. (2023) in their study of urban soil environments in China, found that there is extremely wide variation in both the levels and sources of PTEs pollution. Akinsete et al. (2023) studied the synergistic effects of PAHs and PTEs in urban soils in high traffic areas of Nigeria. In Greece, the cultivation of the Cretan medicinal herb Origanum Dictamnus in urban soil environments in Athens was investigated by Martini et al. (2023), determining the average Ni concentration equal to 12.65 mg·kg^{-1} dry soil. For Co, the highest mean concentration values are in Egypt, followed by North Macedonia. France, Russia, and Serbia show the lowest mean concentration. Shen et al. (2023) conducted a study concerning the determination of HM pollution sources in China. The mean cobalt levels were estimated at 7.9 mg·kg^{-1}, while Petrini et al. (2022) observed the value of 11 mg Co/kg urban soil, showing that the primary pollutant in surface soil are the metals originated from the atmospheric deposition probably produced by metallurgical works. Higher levels of cobalt (28 mg·kg^{-1} dry soil) were detected by Stafilov et al. (2022), after studying the anthropogenic and natural factors influencing HM and PTEs distribution in urban soils of North Macedonia. As for Mn, the highest mean concentration value is in Spain followed by Armenia and the lowest in Croatia and Algeria. Regarding Hg, the highest mean concentration value is by far in Italy, with Greece in second place and Armenia in the third. The countries with the lowest mean values (below 0.5 mg·kg^{-1}) are Russia, Iran, Spain and North Macedonia. Serrani et al. (2022) in their study investigated the heavy metal load in urban soil samples along with their effects on the biochemical properties of urban soils in Italy. Li et al. (2022) found that in urban areas close to industrial regions in Northwest China, the mean Hg concentration was 0.0415 mg·kg^{-1}. To ensure the long-term viability of the city's environment, the researchers came to the general conclusion that the highway environment and the city construction facilities required an improvement, while industrial waste contamination was already under monitoring.

HEAVY METALS CORRELATION TEST

In the various published studies, the results were used for the present meta-analysis, it has been shown that the values of several physicochemical properties correlate either positively or negatively with the values of total and available metal concentrations in urban soils. Papadimou et al. (2023) demonstrated the strong correlation between metal elements of surface soil samples and on soil parameters with a prominent value of soil reaction, i.e. soil pH. Investigations, in which there was a parallel statistic and geostatistical analysis, revealed additional factors influencing the availability and distribution of many minerals. Of particular interest was the study of the relationship between soil pH and the concentrations of both Fe and more toxic Cd (Golia and Diakoloukas 2022). HM and PTEs mean values were used to generate statistical correlation test and PCA plots. Table 3 presents the correlation coefficients at 0.05 or 95% significance level. The blue color depicts positive correlations, while the cells in red color depict negative correlations. The color gradation represents the strength of the correlation, i.e. the strong color indicates a strong correlation between the two variables, while the weak color indicates weak correlations. Strong correlations are observed between Ni and Cr. These metals are significantly positively correlated with each other, as their value is quite close to unity. On the contrary, a negative correlation is observed between Pb and Co.

PRINCIPAL COMPONENT ANALYSIS OF THE DATA

Despite the fact that the correlation analysis performed was the result of statistical processing of mean HM and PTEs concentrations from

Table 3. HM and PTEs correlation test

HM	Pb	Cu	Zn	Cr	Cd	Hg	Ni	Co	Mn
Pb	1	0.12116	0.44927	0.04574	0.56998	0.23932	-0.04626	-0.26476	0.32818
Cu	0.12116	1	0.30498	0.12962	-0.04327	0.00835	0.0586	-0.085	0.37752
Zn	0.44927	0.30498	1	0.1326	0.61317	0.02309	-0.06042	0.17975	0.50957
Cr	0.04574	0.12962	0.1326	1	0.08083	-0.0526	0.85281	-0.11381	0.0454
Cd	0.56998	-0.04327	0.61317	0.08083	1	-0.04428	0.14195	-0.04093	0.25906
Hg	0.23932	0.00835	0.02309	-0.0526	-0.04428	1	-0.08953	-0.03678	0.32275
Ni	-0.04626	0.0586	-0.06042	0.85281	0.14195	-0.08953	1	0.10823	-0.06741
Co	-0.26476	-0.085	0.17975	-0.11381	-0.04093	-0.03678	0.10823	1	-0.10469
Mn	0.32818	0.37752	0.50957	0.0454	0.25906	0.32275	-0.06741	-0.10469	1

different countries and cities, with different microclimate and different anthropogenic habits, the results showed a relationship (positive or negative) between the studied metals. For a more accurate and correct interpretation of the results, principal component analysis (PCA) was implemented. PCA is a frequently used statistical method for the analysis of large data sets accompanied by a large number of features for each observation. Moreover, it is characterized by the continuous rise in the ability to interpret and justify the data by retaining the maximum amount of information but also has the advantage of visualizing multidimensional data. PCA is a statistical method that leads to a reduction of the dimensionality of large volume and difficult to manage data sets. This is performed by linearly transforming the data into a new coordinate system in which (most of) the variance in the data can be expressed with fewer dimensions than the initial data. Many studies employ the first two main components to plot data in two dimensions and visually highlight clusters of closely linked data points (Golia and Diakoloukas, 2022). Figures 2 and 3 were created in the current work utilizing the relevant software. Figure 2 depicts metallic components that are likely to have a common origin in the same region. Furthermore, the countries that are likely to have been polluted by the investigated heavy metals due to the same interactions are provided.

According to Figure 3, Ni and Cr appear to have a shared origin, as they are located in the same quadrant of the PCA graph. The existence of Ni appears to be geochemical since it is found in rocks and minerals in places where appropriate soil sampling has been done (Golia et al., 2021b; Aslanidis & Golia, 2022). There have been numerous studies that show the common presence

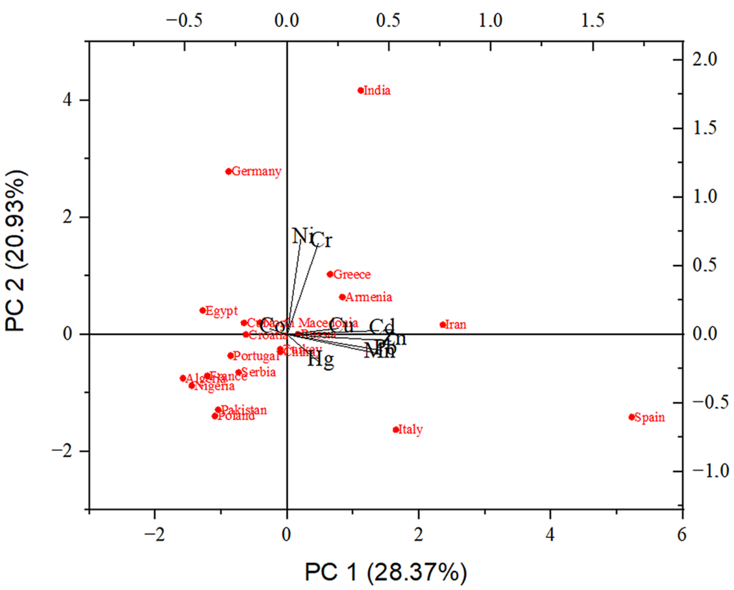

Figure 2. Principal component analysis between HM and PTEs in the selected countries

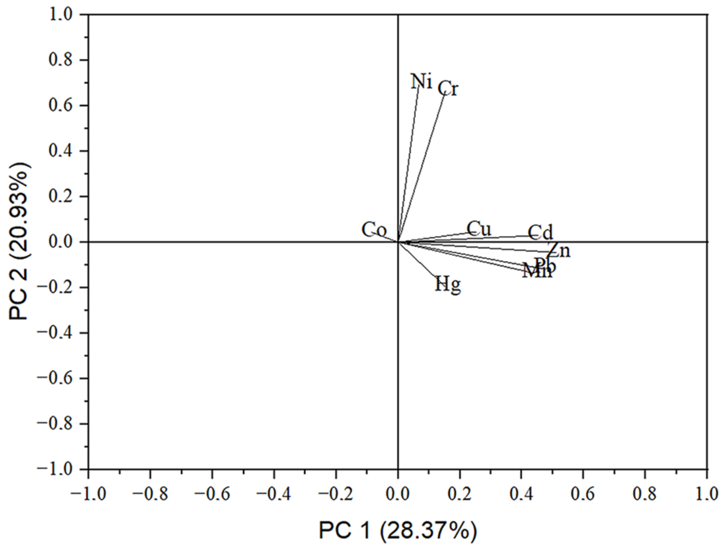

Figure 3. Principal component analysis between the studied HM and PTEs

of Cu, Cd, and Zn. Their presence is primarily owing to the fuels used to heat houses and crafts. Furthermore, they have been observed in train stations because of the persistent friction of the carriage wheels with the rails when the trains slow down and apply the brakes. Furthermore, automobile batteries and materials found in car workshops or other wheeled vehicles contribute to the prevalent and regular occurrence of these metals. According to Silva et al. (2021), car traffic is mostly to blame for anthropogenic pollution in towns with few industrial facilities. Leaded fuels were once the primary Pb source. Despite a recent reduction due to the withdrawal of lead gasoline additives, Pb is still present in soils today. The principal sources of Cr and Ni are automotive brakes and tire wear. However, these two components are likewise highly related to the source material. Several studies (Golia et al., 2021b; Papadimou et al., 2023) have identified this pattern highlighting the multiple factors determining their chemical behavior and reactions within the soil environment.

CONCLUSIONS

In the present study, a review of published papers from 2010 onwards about HM and PTEs contamination levels in urban and peri-urban soils was implemented. A detailed statistical investigation has been conducted, by completing meta-analysis of published data on HM and PTEs pollution in urban soils. The new findings highlight the importance of studying urban soils as they determine an assortment of chain reactions in the soil-plant-water horizon system. Green spaces such as courtyards, parks, and playgrounds are HM accumulation sites that threaten human health. There was an immense variance in metal concentrations across each country tested, which depended on soil physicochemical factors although primarily influenced by anthropogenic activity. The climatic and geographical profile of an area influence HM and PTEs levels and distribution. Significant correlations were found between the studied metals, presumably revealing their common origin.

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