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Estimating remobilization of potentially toxic elements in soil and road dust of an industrialized urban environment

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Abstract The mobility of potentially toxic elements (PTEs) is of paramount concern in urban settings, particularly those affected by industrial activities. Here, contaminated soils and road dusts of the medium-size, industrialized city of Volos, Central Greece, were subjected to single-step extractions (0.43 M HNO_3 and 0.5 M HCl) and the modified BCR sequential extraction procedure. This approach will allow for a better understanding of the geochemical phase partitioning of PTEs and associated risks in urban environmental matrices. Based on single extraction procedures, Pb and Zn exhibited the highest remobilization potential. Of the non-residual phases, the reducible was the most important for Pb, and the oxidizable for Cu and Zn in both media. On the other hand, mobility of Ni, Cr, and Fe was low, as inferred by their dominance into the residual fraction. Interestingly, we found a significant increase of the residual fraction in the road dust samples compared to soils. Carbonate content and organic matter controlled the extractabilities of PTEs in the soil samples. By contrast, for the road dust, magnetic susceptibility exerted the main control on the geochemical partitioning of PTEs. We suggest that anthropogenic particles emitted by heavy industries reside in the residual fraction of the SEP, raising concerns about the assessment of this fraction in terms of origin of PTEs and potential environmental risks. Conclusively, the application of sequential extraction procedures should be complemented with source identification of PTEs with the aim to better estimate

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the remobilization of PHEs in soil and road dust influenced by industrial emissions.

Keywords Sequential extractions · Trace metals · 0.43 M HNO_3 · 0.5 M HCl · Single extractions · Mobility

Introduction

Urban environmental media, such as soil and road dust (also referred to as road-deposited sediments), accumulate significant amounts of trace metals, originating mainly from vehicle emissions (exhaust and non-exhaust), industrial activities, and municipal wastes (Wong et al., 2006). Resulting concern over ecosystem and human health risk is reflected in the scientific literature through the development and testing of methods that target the most available fraction of potentially toxic elements (PTEs). This is the fraction that is available for interaction with the dissolved phase at short time scales, through processes such as sorption/desorption and (surface) precipitation/dissolution reactions (Groenenberg et al., 2017; Kördel et al., 2013; Peijnenburg et al., 2007; Rodrigues et al., 2013, 2018). By contrast, PTEs incorporated in the crystal lattice of minerals, or occluded in particles (oxides, organic matter), will be unavailable for exchange in the soil solution, thus, relatively immobile, and eventually unavailable for uptake by biota (Groenenberg et al., 2017; Kördel et al., 2013).

Several single-step and multiple, sequential-steps extraction procedures (SEP) have been proposed to determine the potential available fraction of metals, also denoted as labile, geochemically reactive or, shortly, reactive (Groenenberg et al., 2017; Tipping et al., 2003). Among the most popular single-step extractions are those including dilute acids, such as 0.43 M HNO_3 and 0.1, or 0.5 M HCl (Groenenberg et al., 2017; Rodrigues et al., 2013; Römkens et al., 2009; Sutherland et al., 2001). The standardized 0.43 M HNO_3 extraction, (BS ISO 17586:2016., n.d), has been developed and validated to enable measurements of the maximum amount of metals that could be released under (predefined) worst-case environmental conditions (Vark & Harmsen, 2015). Similarly, the 0.5 M HCl extraction assumes that trace metals associated with degradable organic matter and with surface coatings of mineral particles would be more available than those in primary minerals or occluded by secondary mineral structures (Sutherland et al., 2001 and references therein). Regarding sequential extractions, they aim at extracting different pools of metals that are susceptible to release from the solid matrix under changing environmental conditions, i.e., changes in the ionic strength of soil solution, pH, Eh, and mineralization of organic matter (Bacon & Davidson, 2008; Tessier et al., 1979).

Although SEPs provide detailed information about the potential mobility of PTEs partitioning in different geochemical phases compared to single-extraction schemes, they are laborious and time-consuming. In this respect, several studies explored how the sum of the potential mobile fractions (e.g., in the modified BCR procedure the sum of the first three fractions) compare with that of single extractions (Kashem et al., 2007; Leleyter et al., 2012; Rao et al., 2010; Sutherland, 2002; Tokalıoğlu & Kartal, 2005). Moreover, soil and dust properties, including pH, grain size distribution, carbonates, and organic matter content, have been found to influence the trace metal geochemical fractionation and mobility (Kelepertzis & Stathopoulou, 2013; Kelepertzis et al., 2015; Rodrigues et al., 2010). Iron, Mn, and Al (oxyhydr)oxides have been also found to exert significant control on the potential mobility of trace metals (Argyraki et al., 2018; Entwistle et al., 2020). The assessment of the magnetic properties of Fe oxides (concentration, mineralogy, and grain-size) can reveal information about the extent, source, and temporal evolution of anthropogenic pollution related to industrial and other human activities (Liu et al., 2012). The strong relationships observed between magnetic susceptibility and PTEs have led to an ever-increasing number of studies that apply environmental magnetism to monitor pollution in both urban soils and road dust (Bourliva et al., 2016; Das et al., 2017; Górka-Kostrubiec et al., 2019; Jordanova et al., 2021; Kelepertzis et al., 2021; Zhang et al., 2012), provided that the local geology does not dominate the anthropogenic signal (Aidona et al., 2016; Blundell et al., 2009; Botsou et al., 2016). Considering the ease, low-cost, and non-destructive nature of magnetic susceptibility measurements, further research is needed to understand the governing relationships between magnetic susceptibility and the potentially mobile fraction of PTEs.

Volos is a medium-sized (about 150,000 inhabitants) industrialized city, located in central Greece (Fig. 1).

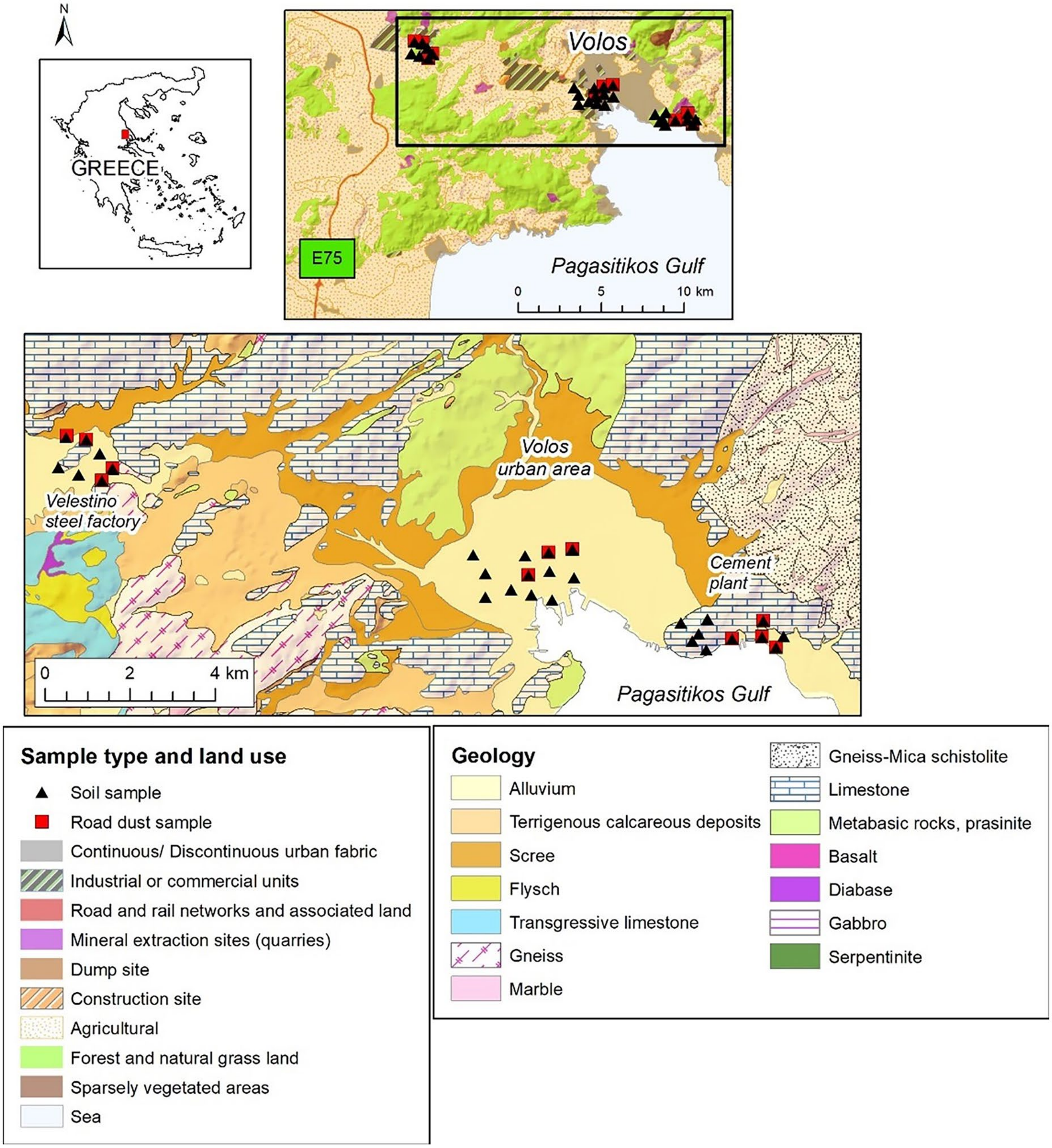


Fig. 1 Geological map of the study area modified after the 1:50,000 geological map of Greece, Volos Sheet (Katsikatsos et al., 1978). Sampling locations and types of samples of the present study are also marked on the map

Industrial activities include a steel plant, located 20 km west of the city, and a cement plant, located about 3 km east of the city center. In our previous publication, we focused on the spatial distribution, the degree of contamination, and the sources of PTEs in soil, road, and house dust samples (Kelepertzis et al., 2020). A subsequent study estimated the bioaccessible fraction of PTEs and found a close association of this fraction with ferrimagnetic phases of anthropogenic origin (Kelepertzis et al., 2021). Motivated by our previous findings, here, we present the geochemical results obtained by applying single and sequential extraction procedures on contaminated soil and road dust samples from the industrial area of Volos. Most of the studies appearing in the scientific literature have investigated the mobility of PTEs in either soils or road dusts, by applying single and/or sequential extraction procedures. Moreover, the majority of studies have targeted to explore the remobilization potential of PTEs in urban areas, not bearing the influence of industrial emissions from steel and cement industries. As a result, few studies have focused on the relationships between PTEs in mobile pools estimated by both single and sequential extraction procedures (SEPs) and the main controlling parameters in contaminated soil and road dusts in urban areas near heavy industrial operations (examples given by Dong et al., 2020; Gabarrón et al., 2019; Sungur et al., 2014). Such information is necessary for improving our understanding of geochemical partitioning of PTEs in soil and road dust to assess their mobility.

The main objectives of the present comprehensive study are to (a) characterize the mobility and geochemical fractionation of PTEs in soil and road dusts, (b) compare the results of single and sequential extraction schemes as effective methods for the estimation of the potentially mobile fraction of the examined elements, and (c) examine the role of magnetic susceptibility and other physicochemical parameters of soil and road dust on the potentially mobile fraction of PTEs.

Materials and methods

Sampling and samples pre-treatment

A total number of 29 soil samples (0–10-cm depth) and 12 road dust samples (Fig. 1) were selected from the sample data set of an earlier survey in the wider area of Volos (Kelepertzis et al., 2020). The criteria for sample selection were the total content of trace metals as determined by the near-total dissolution of soil and dust samples by using a mixture of HNO_3_$HClO_4$_HF. Specifically, we included samples that showed the highest concentrations of trace metals. These samples were located around the steel mills ($n=7$ for soils and $n=5$ for road dusts), the cement plant ($n=10$ for soils and $n=4$ for road dusts), as well as within the city center ($n=12$ for soils and $n=3$ for road dusts). A statistical summary of total PTEs concentrations of soil and road dust samples is given in Table S1. Laboratory sample preparation of the soil and road dust samples included sequential sieving through 2-mm and 100-μm nylon sieves, to focus on the geochemically reactive particles. In addition, rock samples ($n=7$), from representative rock outcrops, and slags ($n=2$), located next to the steel factory at Veles Tino were also included in the analysis for characterizing the geochemical partitioning of the selected elements. Details on sample collection and preparation, and analytical methods for the determination of the near-total PTEs concentrations are described in a previous study (Kelepertzis et al., 2020).

Physicochemical parameters

The soil pH was measured in 1:2.5 soil:water suspesion. The soil texture was determined by the hydrometer method (Gee & Or, 2002). Organic matter (OM) content was determined by the dichromate oxidation procedure (Nelson & Sommers, 2015). Soil calcium carbonate ($CaCO_3$) contents were determined with a calcimeter by measuring the CO_2 volume after acidification of the soil sample. Magnetic susceptibility was measured on the <100 μm fraction of soil and dusts using a Bartington, dual frequency MSB sensor at low (0.465 kHz) and high (4.65 kHz) frequency. Magnetic susceptibility (χ) was expressed on a mass specific basis (10^{-6} m^3 kg^{-1}) (Dearing, 1999). Summary statistics of magnetic susceptibility values are given in Table 1 and have been discussed in a previous study (Kelepertzis et al., 2021).

Single-step and sequential extraction procedures

The soil and road dust samples were processed following two different single-step schemes, using dilute (i) nitric acid (0.43 M HNO_3), and (ii) hydrochloric acid (0.5 M HCl) targeting the potentially available fraction of PTEs. The dilute nitric acid method involved mixing of 1 g of sample with 40 ml of a 0.43 M HNO_3 solution and shaking for 2 h at room temperature. The proposed 1:10 (w:v) ratio of Rodrigues et al. (2010) was modified to ensure that pH values of the final extraction fluids were within the range 0.8–1.0. This was necessary due to the calcareous nature of the soils and road dusts. The dilute hydrochloride acid method consisted of mixing 0.5 g of sample with 10 ml of 0.5 M HCl solution for 1 h at room temperature (Sutherland, 2002). Both extractions were performed

Table 1 Summary statistics of physicochemical parameters of road dust and soil samples

Sample type	Parameter	Mean	Median	Minimum	Maximum	Std. deviation
Road dust	pH	8.0	8.0	7.4	8.9	0.5
	$CaCO_3$ (%)	46.2	51.2	5.9	64.6	18.9
	OM (%)	5.8	5.6	4.0	7.1	0.9
	χ (10^{-6} m^3 kg^{-1})*	10.77	4.27	1.23	44.07	13.59
Soil	pH	7.8	7.8	7.2	8.2	0.2
	$CaCO_3$ (%)	20.4	16.5	3.3	48.3	13.1
	SOM (%)	5.3	5.2	1.6	8.6	1.6
	Sand (%)	54.2	54.6	28.6	74.6	11.0
	Silt (%)	32.8	34.0	18.6	45.2	7.2
	Clay (%)	13.0	10.8	2.5	32.5	6.6
	χ (10^{-6} m^3 kg^{-1})*	1.92	1.12	0.48	9.13	2.04

*Data from Kelepertzis et al. (2021)

in a mechanical shaker. The extracts were separated from the solid residue by centrifugation at 3500 rpm for 10 min, and subsequent filtration through a 0.45-μm filter. The solutions were kept in a refrigerator prior to the analytical determinations.

Concentrations of Cu, Mn, Pb, and Zn in the solutions were determined by flame atomic absorption spectroscopy. Iron, Cr, and Ni were not determined because of their predominant presence in the residual phase (see "Contents and extractabilities of PTEs by single-step and sequential extraction procedures" section). Furthermore, these elements have been previously found to have low bioaccessibility percentages in the same samples (Kelepertzis et al., 2021). Procedural blanks and five analytical duplicates were added to each analytical batch (batches were based on chemical extraction) for quality control purposes. Certified reference materials are not available for these chemical extractions. The relative percent difference (RPD) was calculated for each pair of duplicates as an indication of method precision revealing RPD values lower than 20% for all elements and both extractions, except for Pb in the HNO_3 extractions (mean RPD ~ 23%).

The modified BCR SEP, proposed by the Standards, Measurements and Testing Programme of the European Commission, aims to release into solution in sequence the acid-soluble, the reducible, and oxidizable fractions of metals (Rauret et al., 1999), i.e., the fractions that could be released from the soils under changes of pH, redox potential, and oxidation of organic matter (Bacon & Davidson, 2008; Tessier et al., 1979). More details about the procedure can be found elsewhere (Rauret et al., 1999; Sungur et al., 2021). The soil and road dust samples were subjected to the three-step, modified BCR SEP, applying successive extractions with 0.11 M acetic acid, 0.5 M hydroxylamine hydrochloride in 0.05 M nitric acid (reducing agent), and 1 M ammonium acetate at pH 2 after digestion with 8.8 M hydrogen peroxide (oxidizing agent). An additional step using a HNO_3-HCl mixture was included to dissolve the residue after the three extraction steps. Reagents of analytical purity (Merck, Germany) and deionized water (MilliQ; 18.2 MΩ/cm resistivity) were used throughout the analytical procedures. Plastic utensils and glassware were soaked in 1:1 (v/v) HNO_3:deinonized for 24 h, rinsed with 1% (v/v) HNO_3 and then deionized water prior to use. PTEs (Cr, Cu, Ni, Fe, Mn, Pb, Zn) concentrations were determined by an Analytic Jena Model novAA-350 flame atomic absorption spectrometer (FAAS), equipped with a hollow cathode lamp in an air-acetylene flame. Calibration standards were prepared by appropriate dilutions of single-element stock solutions (SCP SCIENCE, 1000 μg/ml, AA Standard). Detection limits for Cr, Cu, Fe, Mn, Ni, Pb, and Zn were 0.02, 0.03, 0.06, 0.05, 0.03, 0.02, and 0.03 mg kg^{-1} dry weight, respectively. The sum of the four fractions was cross-checked with the element concentrations obtained by the strong acids digestion (HNO_3–$HClO_4$–HF). Recoveries of SEP in relation to the strong acid digestion were (mean ± standard deviation) 62 ± 19% for Cr, 98 ± 10% for Cu, 81 ± 14% for Fe, 97 ± 11% for Mn, 96 ± 10% for Ni, 102 ± 14% for Pb, and 97 ± 13% for Zn. The certified reference material (BCR-701, lake sediment) was used ($n = 4$) to test the accuracy of the procedure and the obtained results are given in Table S2.

Statistical analysis

Statistical analysis was performed with IBM SPSS Statistics version 26. All variables were screened for normality of their statistical distribution by the Shapiro–Wilk test. Because of violations of normality, non-parametric statistical tests were employed. The Spearman-rho correlation coefficient (r_s) was used to explore the relationships between the variables. The Mann–Whitney *U* test and Wilcoxon-rank tests were employed to explore the differences of measured parameters in different independent and related datasets, respectively. The relationships between dilute-acids extractable PTEs contents and the magnetic susceptibility and physicochemical parameters were studied by factor analysis with varimax rotation on log-transformed data. Plotting of geochemical data was performed with OriginPro 2016 (OriginLab Corp.).

Results and discussion

Physicochemical properties of soil and road dust

The summary statistics of physicochemical parameters are given in Table 1. The pH of soil ranged from 7.17 to 8.23, with a mean value of 8.02 (Table 1), reflecting the presence of calcite in bedrock (Kelepertzis et al., 2020). Slightly higher pH values were determined in the road dust samples (range 7.36 to 8.92), but the values were not statistically different (Mann Whitney *U* test, $p > 0.05$). Comparable OM values were measured between the two environmental sampling media (medians 5.64% and 5.22% for the road dust and soil, respectively). In the road dust samples, OM was negatively correlated to pH ($r_{s=} -0.832$; $p = 0.001$), suggesting that organic compounds released from traffic emissions or the use of fertilizers in by-road vegetation contribute to the lowering of dust pH values (Acosta et al., 2015). Nevertheless, a notable enrichment of the road dust with $CaCO_3$ (median 51.2%,) compared to soil samples (median 16.5%), attributed to asphalt concrete abrasion (Pérez et al., 2008; Zannoni et al., 2016), contributes to the buffering capacity of the former. The soil samples exhibited a wide range of clay (2.50 to 32.5%), silt (18.6 to 45.2%), and sand (28.6 to 74.6%) contents, with most samples classified as loam and sandy loam.

Contents and extractabilities of PTEs by single-step and sequential extraction procedures

Table 2 summarizes the results of PTEs contents determined by the two dilute acids extractions. Potentially available PTEs of the soil samples exhibited a wide variation, similarly to their total contents (Table S1), reflecting the influence of both point (steel works, cement plant) and diffuse sources (traffic) of pollution (Kelepertzis et al., 2020). In fact, the potentially available fractions of PTEs followed the distribution of the respective total contents ($r_s = 0.668$–0.973; $p < 0.05$). Thus, extractable PTEs concentrations by the dilute acid procedures are strongly dependent on the total contents in both environmental media.

Calculation of the percentage recoveries of the single-step extractions in relation to total PTEs contents is more relevant when assessing different types of samples (Kelepertzis et al., 2015; Massas et al., 2013), or samples from different areas. The percentage recoveries of PTEs by the 0.43 M HNO_3 extraction in the road dust samples, based on the median values, followed the order Pb (78%) > Zn (67%) > Cu (53%) > Mn (25%) (Table 2). For the soil samples, extractabilities of Pb, Cu, and Zn were significantly lower than the road dust (Mann Whitney *U* test, $p < 0.05$), with medians of 62% (Pb) and ~ 40% (Cu, Zn). Contrarily, the percentage recovery of Mn was higher in the soil samples and accounted for 40% of its total content. Extractabilities of Cu, Mn, and Pb by 0.5 M HCl were significantly higher for the soil (medians ~ 31%, 35%, and 66%, respectively) compared to the road dust (medians ~ 5%, 14%, and 45%, respectively). In the instance of Zn, no statistically significant differences were found between the two environmental media (medians of ~ 34% for both the road dust and soil samples) at the 95% confidence interval.

Despite the observed differences in the extractabilities of PTEs by the two procedures in each medium (further discussed in "Comparison of methods targeting PTEs potentially available fractions" section), the results show that Pb and Zn are the elements with the greatest potential for release from the soil and road dust. Compared to other studies, median recovery of Pb by dilute HNO_3 from the soil is substantially higher than that reported for Porto soils (27%

Table 2 Summary statistics of PTEs contents of the Volos road dust and soil samples extracted by 0.43 M HNO_3 and 0.5 M HCl and their percentage recoveries in relation to total contents

Parameter		**Road dust**					**Soil**				
		Mean	Median	Minimum	Maximum	Std. deviation	Mean	Median	Minimum	Maximum	Std. deviation
PTEs contents (mg kg^{-1})	Cu-HNO_3	56	47	6	175	43	41	18	8	169	45
	Cu-HCl	12	4	2	77	22	32	14	2	143	41
	Mn-HNO_3	478	275	116	1309	469	389	351	230	669	120
	Mn-HCl	293	126	71	1124	357	363	332	94	692	135
	Pb-HNO_3	133	63	36	559	160	93	54	15	418	100
	Pb-HCl	87	33	22	511	144	97	45	20	518	123
	Zn-HNO_3	781	338	118	2310	766	190	83	13	1256	284
	Zn-HCl	591	170	57	2463	806	174	66	11	1088	266
Percentages to total (%)	Cu-HNO_3	55	53	35	74	11	46	40	22	93	17
	Cu-HCl	7	5	3	18	5	33	31	3	75	20
	Mn-HNO_3	25	25	18	36	5	40	40	24	70	10
	Mn-HCl	15	14	9	30	6	37	35	22	60	10
	Pb-HNO_3	79	78	60	101	15	58	62	28	80	14
	Pb-HCl	45	45	21	88	16	62	66	10	94	19
	Zn-HNO_3	81	67	56	139	28	41	37	15	76	17
	Zn-HCl	52	35	13	148	42	36	34	13	81	18

of total Pb) (Rodrigues et al., 2010), and lower than that of Athens soil (76% of total Pb) (Kelepertzis & Argyraki, 2015). For the road dust samples, the median recoveries of Cu, Pb, and Zn by dilute HCl are much lower than those found in Oahu (Hawaii) road dust (61%, 95%, 50% of total contents, respectively) (Sutherland et al., 2001), as well as those from Ontario (92%, 71%, 85% of total contents, respectively) (Stone & Marsalek, 1996).

Summary results of the modified BCR SEP are presented in Fig. 2 and Table 3. The fractions of metals released during the early stages of the procedure (i.e., F1, F2, and F3) have the greatest potential for mobility (Davidson, 2013; Tessier et al., 1979), whereas trace metals found in F4 are generally considered to be environmentally immobile (Leleyter et al., 2012; Madrid et al., 2007). Rather low metal contents were found in the acid-soluble fraction (F1), particularly for Cu, Cr, Fe, Mn, and Ni, accounting for less than 10% of total contents (Fig. 2). The fraction was more important for Pb and Zn, particularly for the road dust samples (Fig. 2b), in which accounted for 12% and 20% of total contents, respectively. In the soils (Fig. 2a), the reducible fraction (F2), was the most important for Pb (51%) and contributed significantly to the partitioning of Mn (28%) and Zn (23%). In the road dust samples, the respective contributions to total contents were 29% for Pb and 20% for Zn. For all other elements, the reducible fraction contributed by less than 10% of total contents in both datasets.

The oxidizable fraction (F3) was the second most important fraction for Cu (18% and 24% of total contents for soil and road dust, respectively), Cr (8% for both matrices), and Ni (9% in soil and 12% in road dust), and for Zn in the soil samples (24%). In the road dust samples (Fig. 2b), the oxidizable fraction accounted for the majority of Zn and contributed by 39% to total contents. Manganese and Fe partitioning into this fraction was low (less than 8% and 2% of total contents, respectively). The residual fraction (F4) was the most abundant for most studied elements. In the soil samples, the contributions of residual fraction to total contents were (medians): Fe (96%), Cr (82%), Ni (79%), Cu (66%), Mn (52%), Zn (40%), and Pb (21%). In the dust samples, the respective percentages were Fe (98%), Cr (86%), Mn (80%), Ni (73%), Cu (55%), Pb (32%), and Zn (25%). Thus, in both datasets, the most labile metals were Pb and Zn, that have been shown to be of anthropogenic origin in the study area (Kelepertzis et al., 2020, 2021). Previous studies also argued for the dominance of Cr, Fe, and Ni in residual phases, both in soil and road dust studies (Botsou et al., 2016; Dong et al., 2020; Jayarathne et al., 2018).

Comparing the relative percentages of the residual fraction (F4) to total contents between the two types of samples, it was found that the values of Fe, Mn, and Pb were higher in the road dust than in the soil samples (Fig. 3). The increase of the residual fraction in the road dust samples compared to soils could be largely explained by the higher concentration of magnetite in the former, as inferred by magnetic susceptibility measurements (Table 1) and further elaborated in "Effects on PTEs extracted by the sequential extraction" section.

Comparison of methods targeting PTEs potentially available fractions

The percentage recoveries of the dilute HNO_3, the dilute HCl, and the sum of acid soluble, reducible, and oxidizable fractions of the SEP ($\Sigma_{(F1\text{-}F3)\%}$) within the same environmental medium were compared through a two-tier approach; firstly, by the Wilcoxon test to examine the differences among the variables, and secondly, by bivariate correlation coefficients to examine the inter-variable associations. The results of the tests for Cu, Mn, Pb, and Zn are graphically presented in Fig. 4.

No common ranking with respect to PTEs percentage recoveries was discerned by the methods used. The results were dependent on the environmental medium and the element in question. For the soil samples, a generalized pattern is that the 3-step SEP extracted more Mn, Pb, and Zn relative to total contents than the single-step extractions ($p < 0.05$). In the case of Cu, the percentage recoveries by the 0.43 M HNO_3 extraction were higher than the 3-step SEP, whereas no statistically significant difference was found between SEP and the 0.5 M HCl extraction (Fig. 4a). Comparison of the two single-step extractions showed that the dilute HNO_3 procedure yielded (a) higher recoveries for Cu and Mn, (b) similar for Zn, and (c) slightly lower for Pb compared to the dilute HCl extraction. Strong positive correlations were observed for Cu, Mn, and Zn, with Spearman's rho correlation coefficient ranging from 0.788 to 0.907 between the 3-step SEP and

Fig. 2 Fractionation of PTEs in soil and road dust among the acid soluble (F1), reducible (F2), oxidizable (F3), and residual (F4) fractions in relation to total contents

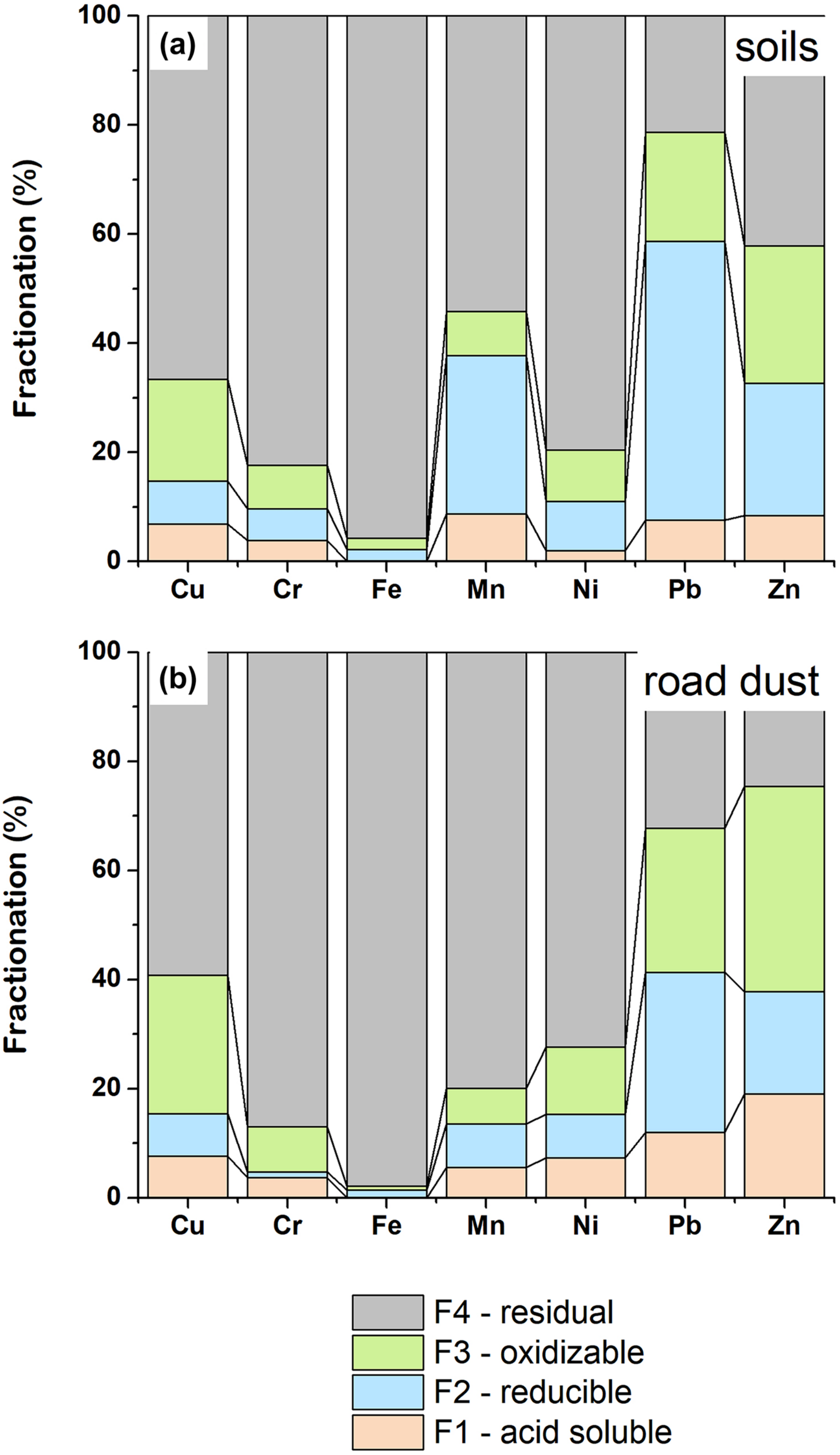


Table 3 PTEs contents (in mg kg^{-1}) of the acid-soluble (F1), reducible (F2), oxidizable (F3), and residual (F4) fraction of the sequential extraction procedure in soil and road dust

PTEs	Fraction	**Road dust**					**Soil**				
		Mean	Median	Minimum	Maximum	Std. deviation	Mean	Median	Minimum	Maximum	Std. deviation
Cu	F1	6.00	5.30	4.00	12.8	2.40	4.01	3.80	2.50	7.10	1.07
	F2	8.03	8.20	2.30	23.4	5.69	6.28	3.80	2.20	27.0	6.50
	F3	29.1	22.0	9.00	66.0	17.4	20.2	6.60	0.50	101	24.9
	F4	82.7	37.0	16.0	395	110	39.9	36.0	11.0	152	24.3
Cr	F1	8.00	8.030	5.47	10.8	1.86	3.91	3.50	bdl	10.6	3.00
	F2	5.44	5.235	bdl	14.8	5.27	6.12	6.42	bdl	10.9	3.81
	F3	16.4	15.7	11.9	21.4	2.970	10.7	8.09	2.73	48.2	8.66
	F4	337	158	53	1099	374	103	87.2	46.0	240	51.3
Fe	F1	10.94	12.59	2.52	20	5.553	7.94	7.86	2.67	13.8	2.58
	F2	505	323	149	1366	376	644	630	116	1723	346
	F3	247	155	44	862	245	646	679	68	1628	357
	F4	30,257	17,706	8439	92,850	25,110	25,989	26,865	8775	40,380	7246
Mn	F1	97.5	59.7	35.0	227.0	71.7	90.4	88.6	41.0	278	46.2
	F2	158	105	27.6	473	141	264	268	91.7	578	103
	F3	132	58.6	33.7	348	126	79.5	76.4	39.0	139	28.460
	F4	1551	871	320	4240	1540	513	476	170	1052	262
Ni	F1	6.84	6.70	5.62	8.23	0.86	2.74	2.35	bdl	5.78	1.567
	F2	8.65	7.50	5.30	16.6	3.21	11.8	9.84	6.05	29.0	6.005
	F3	12.3	12.2	8.44	17.0	2.38	10.8	10.44	3.51	28.1	4.972
	F4	77.2	73.0	32.0	139	28.6	103	85.0	33.0	218	46.8
Pb	F1	11.7	10.7	8.00	26.0	4.87	8.52	8.00	2.00	21.0	4.24
	F2	34.6	23.6	21.0	105	25.3	69.1	45.0	24.00	301	69.9
	F3	35.1	22.9	12.0	112	35.1	32.7	19.0	3.00	210	44.3
	F4	56.0	25.1	10.9	218	67.0	31.7	20.0	11.00	131	26.3
Zn	F1	146	107	28.0	415	120	45.0	17.0	3.00	264	66.5
	F2	153	108	38.0	351	102	76.0	47.0	5.00	278	80.7
	F3	251	220	86.0	480	123	94.0	56.0	11.00	383	94.2
	F4	182	115	53.0	490	154	113.0	79.0	53.0	346	72.5

bdl below detection limit

dilute HNO_3 method, from 0.601 to 0.830 between the 3-step SEP and the dilute HCl method and from 0.548 to 0.644 between the two single-step extractions (Fig. 4b).

Interestingly, a lack of correlation of percentage recoveries for Pb among the three methods was observed (Fig. 4b). Furthermore, extraction by 0.5 M HCl was more aggressive than by 0.43 M HNO_3 (Fig. 4a). This contrasts with the findings of Römkens et al. (2009) reporting that Pb extracted by 0.43 M HNO_3 was almost two times higher than the amount extracted by 0.1 M HCl. Additionally, Cuvier et al. (2021) found a low percentage recovery of Pb by the 0.5 N HCl extraction, which was ascribed to precipitation of Pb as $PbCl_2$, during the extraction procedure. To understand why our results contradict previous findings, we examined in detail the soil samples in relation to their location (Fig. S1 in Supplementary Material). The soil samples obtained from the city center yielded systematically lower percentage recoveries for the dilute HNO_3 leach compared to dilute HCl, while a greater scatter of relative differences was found for the soil samples in close vicinity to the cement plant and to a lesser extent, the steel mills. Obviously, there should be some Pb-bearing phases that can be readily leached by dilute HCl, but not by dilute HNO_3 in the soil samples within the city

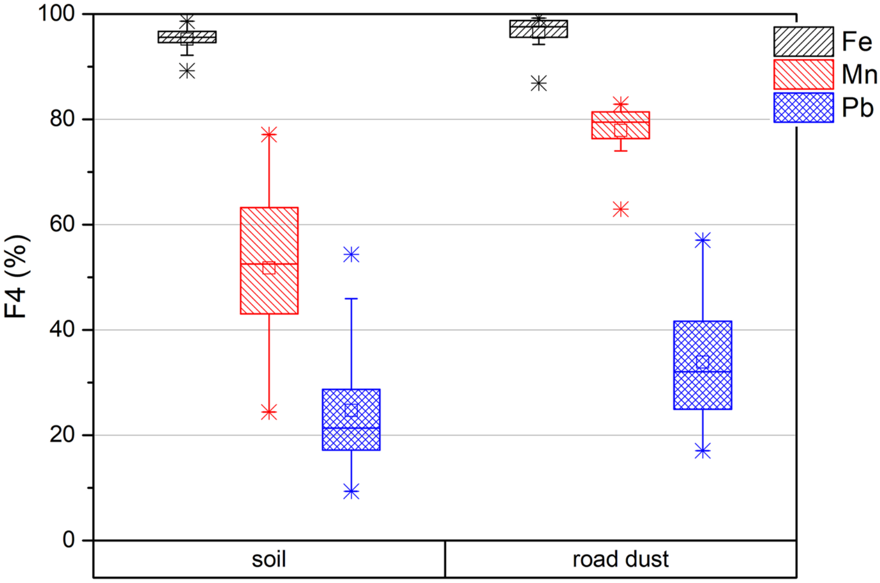


Fig. 3 Comparison of the relative percentages of the residual fraction to total contents of Fe, Mn, and Pb in soil and road dust

center, for instance Pb-sulfide phases, but certainly this hypothesis needs further investigation.

For the road dust samples, the 3-step SEP was more aggressive than the 0.5 N HCl extraction (Fig. 4a), while the dilute HNO_3 was more aggressive than the dilute HCl extraction for all studied PTEs (Cu, Mn, Pb, Zn). Comparison of the 3-step SEP and the dilute HNO_3 yielded element specific results: For Cu and Mn, percentage recoveries by the 3-step SEP were lower than the dilute HNO_3, whereas those of Pb and Zn were similar (Fig. 4a). Furthermore, positive correlation between the two single-step extractions ($r = 0.767$; $p < 0.01$) was found only for Zn (Fig. 4c), while positive correlation between the 3-step SEP and the dilute HNO_3 ($r = 0.603$; $p \leq 0.05$) was found only for Cu.

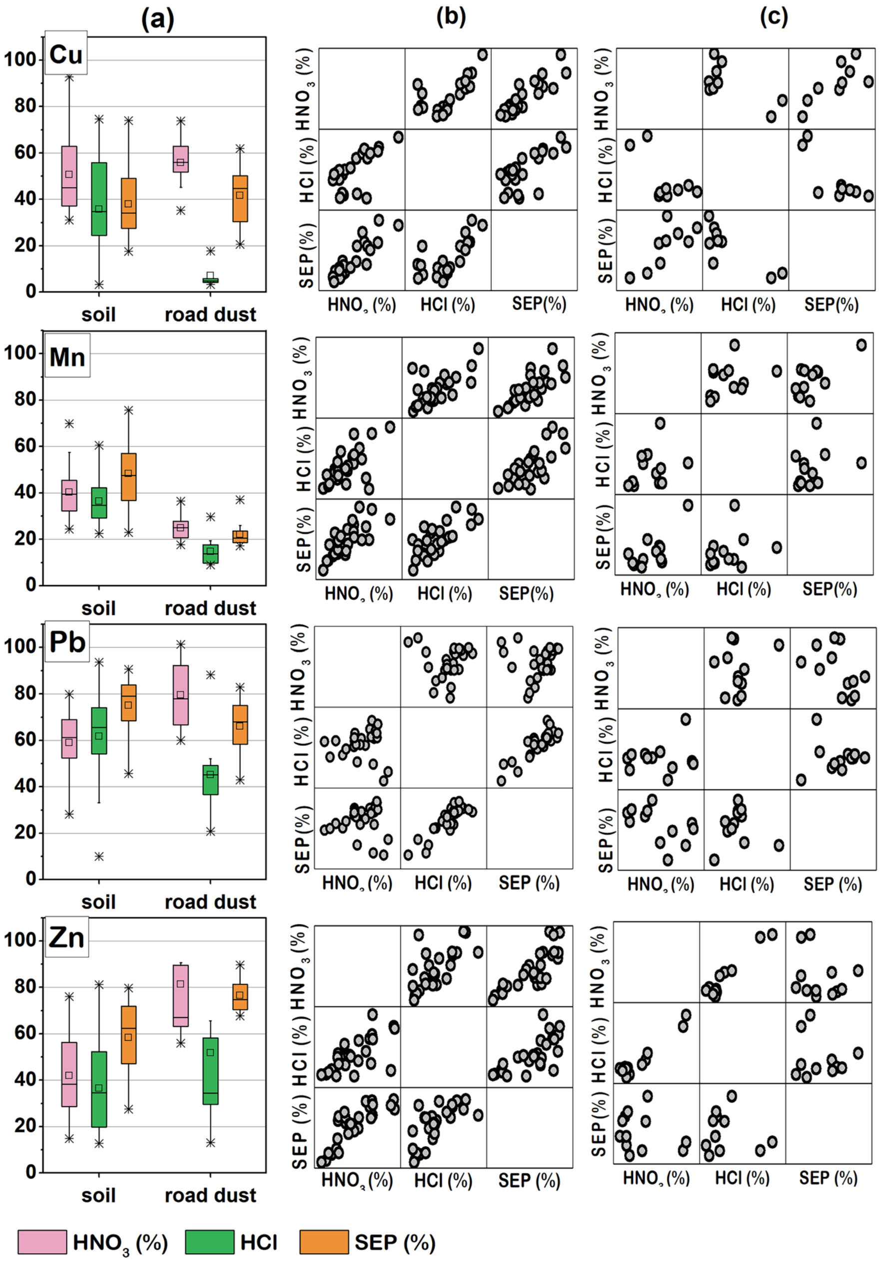
The role of soil and road dust’ physicochemical parameters

Effects on PTEs extracted by single-step extractions

To explore the relationships between the physicochemical properties of the soil and the potentially available fraction of PTEs assessed by the single-step extractions, factor analysis (FA) was conducted (Table 4). The properties tested included pH, OM and carbonate contents, clay as indicator of grain-size distribution, total Al as an indicator of aluminosilicate minerals that may act as scavengers for PTEs (Entwistle et al., 2020), and magnetic susceptibility as a proxy to ferrimagnetic minerals and phases (Botsou et al., 2020; Scoullos et al., 2014; Thompson & Oldfield, 1986). Total Al and magnetic susceptibility of the samples were previously measured by Kelepertzis et al. (2020) and Kelepertzis et al. (2021), respectively.

The analysis revealed four factors that explained 79.6% of the total variance. The first factor (F1, 28.6% of total variance) showed negative loadings for pH and carbonate contents and positive loadings for Al, and the extractability of Cu, Pb, and Zn by 0.5 M HCl (Table 4). Considering that Al is a structural component of aluminosilicate phases, the positive correlation of PTEs extractabilities and Al within F1 could signify their role as substrate-binding sites for these elements through adsorption processes. The inverse relationship of F1 with carbonates could signify a dilution effect of aluminosilicate phases caused by (artificial or geogenic) carbonates. Thus, F1 shows that enrichment of soil with carbonates, (which increased soil pH values and diluted the signal of aluminosilicate phases), resulted in lower percentage recoveries of Cu, Pb, and Zn by dilute HCl compared to total contents (Table 2). Interestingly, no correlation was found between the HCl extractable Pb, Cu, and Zn with OM, contrary to the results reported by Madrid et al. (2007).

Fig. 4 (**a**) Comparative percentage recoveries of Cu, Mn, Pb, and Zn in relation to total contents by single-step and sequential extractions (SEP), and matrix correlation in (**b**) the soil and (**c**) the road dust samples



Factor F2 (26.6%) showed positive loadings for OM and the extractability of Cu, Pb, and Zn by dilute HNO_3, and negative loading for clay. The inverse relationship of clay with OM could be ascribed to the presence of coarse-grained organic matter debris of non-mature soils, or organic coatings on coarser grains. Thus, F2 suggests that organic matter increases the extractability of Cu, Pb, and Zn by dilute HNO_3. Furthermore, the fact that FA grouped HCl and HNO_3 extractabilities into two different factors implies that the solid phases in which Cu, Pb, and Zn are bound are susceptible to dissolution by the two extractants to different degrees, and that organic phases are more effectively extracted by HNO_3 rather than by HCl. Unlike HNO_3, HCl is a weakly reducing acid and is not generally used to digest organic materials (Hu & Qi, 2014).

Table 4 Factor analysis after varimax rotation

Variable	F1	F2	F3	F4
pH	**−0.566**	−0.010	0.181	0.071
Al	**0.845**	−0.355	0.033	0.023
χ	0.011	0.059	−0.081	**0.944**
OM	0.089	**0.746**	0.309	0.194
$CaCO_3$	**−0.886**	0.221	−0.135	0.119
Clay	0.133	**−0.793**	0.344	0.070
Cu-HNO_3	0.135	**0.863**	−0.167	−0.275
Cu-HCl	**0.844**	0.432	−0.065	−0.021
Pb-HNO_3	−0.098	**0.717**	−0.259	0.335
Pb-HCl	**0.818**	0.211	0.122	0.280
Mn-HNO_3	−0.550	−0.073	**0.746**	−0.054
Mn-HCl	0.169	−0.287	**0.895**	−0.134
Zn-HNO_3	0.080	**0.743**	−0.180	0.454
Zn-HCl	**0.642**	0.475	−0.116	0.427

HNO_3 and HCl represent percentage recoveries to total contents

Significant loadings are indicated in bold

Factor F3 (12.8%) exhibited high positive loadings for extractabilities of Mn by both procedures, suggesting the non-selectivity of the two solutions towards Mn-bearing phases. Finally, F4 accounted for 11.6% of the variability and was associated only with χ, implying that magnetic susceptibility did not increase or decrease the extractabilities of the studied elements.

For the road dust samples, instead of FA, the respective relationships were explored through the correlation matrix, due to the small size of the data set. Within this data set, the extractability of Cu by HCl showed positive correlation with magnetic susceptibility ($r_s = 0.733$; $p = 0.010$; Table S3), suggesting that the higher the concentration of magnetite-like phases, the higher the proportion of Cu in relation to its total content that is extracted by HCl. Such a relationship suggests that magnetic phases (magnetite and metallic iron) are a preferable substrate for Cu, in accordance with the findings of Jordanova et al. (2021). Apart from this, no other correlations were found.

Effects on PTEs extracted by the sequential extraction

Even though the applied SEP does not target specific geochemical phases, correlation analysis between PTEs fractions and soil and road dust properties could provide some insight into elemental associations (Bäckström et al., 2004).

Acid soluble fraction: In the soil samples, the extractability of Pb in the acid-soluble fraction increased with an increase of carbonate contents ($r_s = 0.583$; $p < 0.01$; Table S3). The association of Pb with calcite particles, either geogenic or formed from human artifacts, has been previously reported (Howard et al., 2013). Contrarily, no such relationship was found for the road dust samples. Instead, the acid-soluble Pb percentages in the road dust samples were negatively correlated with magnetic susceptibility ($r_s = -0.760$; $p < 0.01$; Table S3), suggesting that as the abundance of magnetic phases increased, the less important the F1 fraction became for the partitioning of Pb. Positive correlations were found between the carbonate content in soils with Cr ($r_s = 0.641$, $p < 0.05$), Fe ($r_s = 0.519$, $p < 0.05$), and Ni ($r_s = 0.723$, $p < 0.05$), implying that these elements were partly released from the dissolution of carbonates.

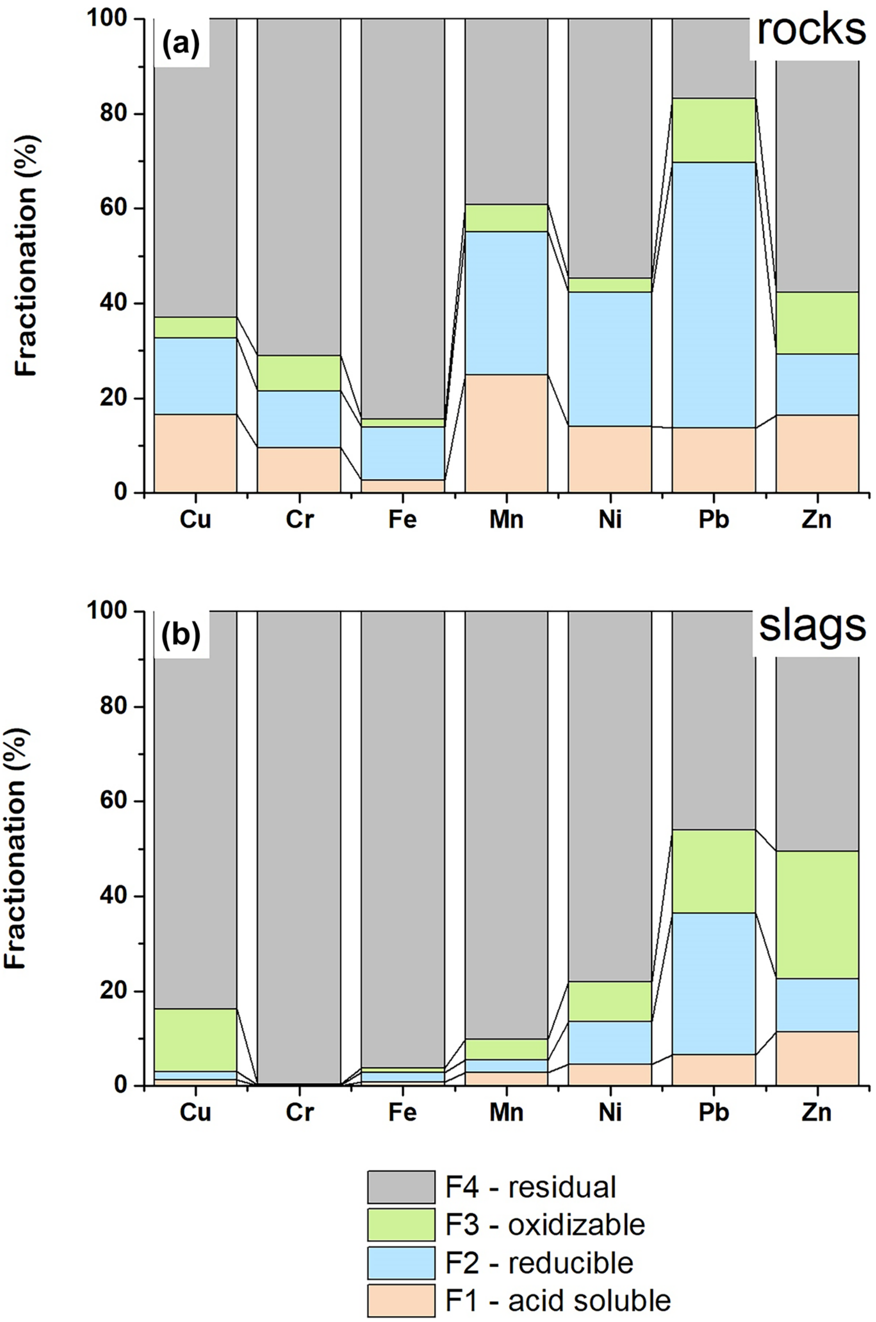
Reducible fraction: The percentages of the reducible fractions of Fe and Ni in the road dust samples were negatively correlated with magnetic susceptibility ($r_s = -0.606$; $p < 0.05$ and $r_s = -0.682$; $p < 0.05$, respectively; Table S3), suggesting that as the abundance of magnetic phases increased, the less important the F2 fraction became for the partitioning of these elements.

Oxidizable fraction: Strong positive correlations were found between OM contents of soil and the percentages of the oxidizable fraction of all metals but Mn, with Spearman correlation coefficient ranging from 0.477 to 0.632 (Table S3), suggesting that the availability of OM increases metal-OM preferable associations. For the road dust samples, similar relationships were encountered only for Pb, which is positively correlated with SOM ($r_s = 0.634$, $p < 0.01$).

Residual fraction: Statistically significant correlation coefficients between magnetic susceptibility and residual Fe ($r_s = 0.678$, $p < 0.01$), Mn ($r_s = 0.695$, $p < 0.01$), Ni ($r_s = 0.709$, $p < 0.01$), Cr ($r_s = 0.823$, $p < 0.05$), Cu ($r_s = 0.875$, $p < 0.05$), and Pb ($r_s = 0.762$, $p < 0.05$) percentages were found in the road dust samples, but not in the soil samples (Table S3). It should be noted that the hydroxylamine hydrochloride solution used to extract the reducible fraction, only minimally attacks magnetite (Poulton & Canfield, 2005; Slotznick et al., 2020), thus, the major part of this oxide is extracted in the F4 step of the procedure. The observed relationships between χ and elements' recovery percentages of the residual fraction suggest that the higher the concentration of magnetic minerals and phases in the road dust, the more important the residual fraction becomes for these elements. It is noted that such anthropogenic magnetite-like particles have been previously identified in the road dust samples by electron microscopy observations (Kelepertzis et al., 2021).

This finding is important because the residual fraction is considered relatively immobile in the environment, thus, of low bioavailability and toxicity (Gope et al., 2017; Jayarathne et al., 2018; Madrid et al., 2007; Trojanowska & Świetlik, 2020). However, magnetite

Fig. 5 Fractionation of PTEs in rock and slag samples among the acid soluble (F1), reducible (F2), oxidizable (F3), and residual (F4) fractions in relation to total contents



particles, particularly the finer ones that contain redox-active Fe, may pose a threat to human health due to their bioreactivity, their ability to penetrate every organ, including the placenta and brain, and have been linked with neurodegenerative cardiovascular diseases (Gonet & Maher, 2019; Gonet et al., 2021; Maher et al., 2016). Further health risks arise from the association to magnetite particles of other bio-reactive metals or organic pollutants (Hofman et al., 2020; Ojha et al., 2015).

Another implication is that the residual fraction is erroneously attributed to geogenic sources solely, in agreement with the findings of Liu et al. (2019). In fact, elements of geogenic origin (i.e., Fe, Mn, Cr, Ni) could be partitioned both in non-residual and residual fractions, while as previously shown, elements of anthropogenic origin (i.e., Pb, Zn, Cu) may be partitioned in residual phases. Supportive to this argument is the geochemical fractionation of seven rock samples, outcropping in the studied area, and two slag samples, produced as by-product of the steel making process, presented in Fig. 5. In the rock samples, the non-residual fractions of the studied elements contributed by 10 (for Fe) up to 84% (for Pb) to total contents (median values), while in the slag samples, the residual fractions contributed as much as 46 (for Pb) to 100% (for Cr) to total contents.

Conclusions

As a response to the increased concern of ecosystem and health-risk hazards arising from expansion of urban settings, often in close vicinity to industrial areas, several methods for assessing the remobilization potential of PTEs in road dust and urban soil have been developed and proposed. Here, we assessed the potential mobility of PTEs in road dust and soil samples from the industrialized city of Volos by employing the dilute HNO_3 and HCl single-step extractions and the so-called modified BCR procedure and discussed the within-and-between differences of methods and studied media.

Road dust and soil of urban settings have distinct composition and physicochemical properties that largely control the remobilization potential and geochemical fractionation of PTEs. We found that anthropogenic Pb and Zn are the most labile elements for both soils and dusts, whereas geogenic Cr, Fe, Mn, and Ni principally reside in the residual fraction of both media. The major influencing factors of PTEs availability were found to be carbonate and organic carbon contents for the soil samples, and magnetic minerals and phases for the road dust samples. In our study, by-products of steel plants (slags), and magnetite-like phases, originating from traffic and industrial emissions, contribute to the residual fraction of PTEs. Thus, the results of sequential extractions could not be considered as indicative of the origin of PTEs. Considering that magnetite-like phases could also serve as a substrate for other toxicants, too, the so-called inert fraction of sequential extractions needs careful consideration to be considered benign in health risk-assessments. The results of this study may assist local stakeholders to consider the remobilization potential of PTEs as one of the evaluation criteria in the environmental risk assessment for each site, with the aim to obtain detailed scientific information about the geochemical behavior of PTEs in urban environmental matrices.

Data availability and material All data generated during this study are included in the article.

Declarations

Competing interests The authors declare no competing interests.

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