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SOIL DEGRADATION CONTROL, REMEDIATION AND RECLAMATION

Trace metal extractability and bioaccessibility in urban soils

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Abstract

Purpose One of the most challenging issues in urban soils is the accumulation of pollutants such as heavy metals, which could reach the natural waters or enter the food chain through plant uptake. In order to assess the health risk related it is necessary to know their availability.

Methods We analyzed the chemical extractability of five trace metals (Pb, Cu, Zn, Ni and Cr) in 55 soils from Santiago de Compostela (Spain) with diverse land use (urban grassland, urban forest, urban agriculture) and parent material lithology (granite, schist, gneiss, amphibolite). Soluble metals were evaluated using an extraction with 0.01 M $CaCl_2$, plant-available metals were obtained after extraction with EDTA, and bioaccessibility was assessed following the USEPA in vitro extraction with glycine.

Results Metal extractability was in general higher in the USEPA method than in EDTA, and much higher than in $CaCl_2$. Among the elements studied, only Zn was detected consistently in $CaCl_2$ extract, with values always lower than 3% of the total contents, in a decreasing sequence Zn > Pb > Ni > Cu > Cr. Concentrations of plant-available metals followed a decreasing sequence Pb > Cu > Zn > Ni > Cr, with values that represented, on average, between 1 and 23% of their total concentrations. Bioaccessibility followed a similar sequence: Pb > Cu > Zn > Ni > Cr, with values that ranged between 2 and 55% of the total concentrations. Plant-available and bioaccessible Cu and Zn were higher in urban garden soils with respect to other uses.

Conclusion The availability of trace metals in these soils is very low and supports previous hypotheses about their sources, with Cu, Pb and Zn coming from anthropogenic pollution and Ni and Cr from natural sources related to the soils parent material.

Keywords Urban soil · Pollution · Metals · Bioavailability · Bioaccessibility · Technosols

1 Introduction

Soil is a fundamental component of urban ecosystems with important functions such as infiltration of water, reducing the risk of flooding, control of air pollution and climate and supply of recreation areas, water and food (Morel et al. 2015). Urban areas cover only about 3% of global land surface (Nieuwenhuijsen 2024), but 55% of human population lived in these areas in 2018, and this number is expected to increase up to 68% in 2050 (UN DESA 2019). The expansion of cities and the increase of the industrialization can negatively affect urban soils ecosystem functions. In urban sites the natural ecosystems change due to anthropogenic activities and one evident impact is soil sealing, leading to changes in hydrological cycling and energy balance. Another great challenge, derived from human activities in cities, is the contribution of polluting substances to the soil, such as emissions from fossil fuel combustion, waste disposal or pesticide use, which can lead to ecological impacts if they transfer to other environmental compartments, but also affect human health by skin contact, inhalation or ingestion if pollutants enter the food chain (Ajmone-Marsan and Biasioli 2010; Li et al. 2018).

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Enrichment in pollutants with respect to non-urban areas is a specific feature of soils in most cities, so significant levels of pollutants can be expected in urban soils (Li et al. 2020). In recent years, home gardening and urban agriculture have become important for food production in cities, but soil contamination must be addressed to ensure food security (Lal 2020). In this sense, it is important to evaluate the mobility of soil pollutants, since only a fraction of the total content is mobile and available for plant uptake and human ingestion (Luo et al. 2012a). Among the most common contaminants present in urban soils are heavy metals, inorganic substances that are non-degradable, difficult to remove and become toxic at high concentrations (Li et al. 2018). Abundant research deals with total trace metal contents in soils, which are regulated in many countries, but potentially toxic elements can be found in different chemical forms, with the soluble and mobile forms being the most worrying and, therefore, is important to increase the research in these fraction of the pollutants (López-Mateo et al. 2023). This is necessary in order to evaluate the risk of transfer to other compartments of the urban ecosystem, such as groundwater or vegetation (Ajmone-Marsan and Biasioli 2010). Moreover, urban soils also happen in public parks and recreational areas where people spend their free time. Exposure to potentially toxic elements can lead to metal intake via inhalation, ingestion or dermal contact (Różański et al. 2018), deriving in health problems such as damage in the liver or the kidney, respiratory diseases or endocrine disruption, which become more dangerous when people are exposed to different types of pollutants simultaneously (Beroigui et al. 2020). Although both adults and children can be exposed to contaminated soils, children are especially susceptible due to higher hand-to-mouth contacts or by eating food from the ground (Wang et al. 2018; Różański et al. 2018).

Different types of chemical extractions are usually employed to evaluate the degree of mobility of these contaminants, the same as in the regular approaches to polluted non-urban soil, assuming that the extracted metals are mobile and could be taken by plant roots and enter the food chain. Among the most used extractions are salt solutions such as $CaCl_2$, useful to assess the immediately available fraction of trace metals, or complexing agents such as EDTA, useful to determine the fraction available for plant uptake (Luo et al. 2012a; Silva et al. 2020). Regarding bioaccessible metals, that is, the fraction of trace metals that are dissolved and absorbed by the gastrointestinal tract, they can be assessed by in vitro or in vivo methods. However, in vivo methods are time-consuming, expensive and present some ethical issues, that is why in vitro methods, which have been fully validated, are nowadays usually employed (Du et al. 2020; Shentu et al. 2023). The use of the three extraction methods together provides complementary information about mobile forms of trace metals, which is important to address environmental and health risk, and is also useful to understand sources of pollution, in addition to the information derived from total element analyses. Trace metals are common pollutants in urban soils, so their total content and mobility have been studied in both small and large cities, more or less industrialized, from countries such as China (Yutong et al. 2016), Spain (Izquierdo et al. 2015), Ghana (Darko et al. 2017), Italy (Madrid et al. 2008) or the United Kingdom (Crispo et al. 2021). In the last years, Wang et al. (2018), Ai et al. (2019), Beroigui et al. (2020) or Shentu et al. (2023) have conducted research assessing human health risk derived from trace metals in urban soils, and geo-accumulation indexes were calculated for different cities in Poland (Różański et al. 2018; Plak et al. 2025) or Portugal (Silva et al. 2021), suggesting increasing concern about this issue. In any case, in Spain, urban soil pollutants remain still unknown in most cities.

The present work is part of a comprehensive research project studying the morphology and physical, chemical and biochemical properties of urban soils in the city of Santiago de Compostela, in northern Spain. Here, we present results of extractability of five trace metals potentially dangerous for human health -lead, copper, zinc, nickel and chromium- in surface samples of 55 soils with different land uses and lithologies. The aim of this study was to know more about their potential risk for human health, by determining the mobility and availability of these elements. Our specific objectives were: (1) to evaluate the soluble fraction, that is, the immediately available fraction of the five studied trace elements using a $CaCl_2$ solution; (2) to evaluate the elements available for plant root uptake determining their extractability in an EDTA solution; and (3) to evaluate their bioaccessibility, that is, the fraction that could be absorbed for the human gastrointestinal tract, following the USEPA method. Our hypothesis is that Pb, Cu and Zn will be the elements with the highest concentrations in all the extractions, due to their anthropogenic origin. In contrast, we expect low extractability of Ni and Cr, which are more related to lithology than to anthropogenic pollution in our context.

2 Materials and methods

2.1 Study area

The municipality of Santiago de Compostela is located in the northwestern corner of the Iberian Peninsula (42º53’N, 8º32’W), with a surface of 222 km^2 and 97,000 inhabitants. The city has an oceanic climate, warm and wet. According to the Köppen−Geiger Climate Classification, it is located in the temperate oceanic climate (Cfb) zone (Kottek et al. 2006). The mean annual air temperature is 13.0 °C, with August as the warmest month (mean air temperature 19 °C) and January the coldest (mean air temperature 8 °C). The average annual precipitation is 1787 mm. The relatively low values for potential evapotranspiration (<300 mm in summer and 50–100 mm in winter) result in a positive water balance (600–800 mm) (Martínez Cortizas and Pérez Alberti 1999). The city presents four main lithological units: (1) granitic rocks, mostly medium- to coarse-grained two-mica granites; (2) Santiago schists, rich in micas and poor in quartz; (3) orthogneisses, with a similar composition to granites; and (4) amphibolites, composed mainly of amphibole and plagioclase.

Urban soils in Santiago de Compostela comprise soils with different degrees of artificialization: former natural and agricultural soils that have been encircled within the city during urban growth and preserved with little modification, soils constructed with human-altered and transported materials, where the original soil has been removed and/or buried by excavated materials, and soils that have been sealed by pavement or concrete for the construction of urban infrastructures. The dominant soils in the city are classified as Umbric Leptosols, Leptic, Haplic and Cambic Umbrisols, Skeletic Transportic Regosols, and Urbic and Ekranic Technosols (Paradelo et al. 2022).

2.2 Soil samples and analyses

Fifty-five soil samples were used as in our previous work (Herbón et al. 2021): composite samples taken with an Edelmann auger (soil depth 0–20 cm) in 55 points randomly selected which are representative of the land use and lithology diversity of the city (Fig. 1). Since grasslands are the most common surfaces in urban parks in Santiago, most soils of the set correspond to this land use ($n = 28$), followed by urban forest areas ($n = 13$) and urban gardens and periurban agriculture soils ($n = 14$). Regarding lithology, 44% of the sampling sites were on schist, 14% on granite, 11% on granite mixed with schist, 24% on gneiss and 7% on amphibolites. The soils were generally acidic, coarse-textured (dominant texture was sandy loam), and rich in organic matter, with differences in soil composition and chemical properties due to the diversity of parent materials and land uses (Paradelo et al. 2021). Soils developed over amphibolites presented heavier textures and greater amounts of iron compounds than soils developed over schist, gneiss, or granite. Among land uses, soils of urban gardens presented higher nutrient content, pH, and salinity than soils of urban forests or urban grasslands (Paradelo et al. 2021). In all cases soils presented heterogeneous microbial communities and activity controlled by organic matter content (Gómez-Brandón et al. 2022).

Regarding inorganic pollutants, total concentrations of the five trace elements have been reported in Herbón et al. (2021) and follow the sequence Zn (55–484 mg kg^{-1}) > Pb (20–566 mg kg^{-1}) > Cr (17–277 mg kg^{-1}) > Cu (17–188 mg kg^{-1}) > Ni (11–91 mg kg^{-1}), with concentrations that are in general higher than in the non-urban soils of the region and regional backgrounds, which are: 55 mg kg^{-1} for Pb, 45 mg kg^{-1} for Cu, 100 mg kg^{-1} for Zn, 65 mg kg^{-1} for Ni and 80 mg kg^{-1} for Cr. According to the geoaccumulation index (Muller 1969), 37% of the soils are classified in the categories ‘uncontaminated’ or ‘uncontaminated to moderately contaminated’ and only 5% of the soils are classified as ‘heavily contaminated’. The elements with the highest enrichment were Pb and Cu, whereas the element with the lowest enrichment was Ni. Total concentrations of organic pollutants have been reported in Paradelo et al. (2023), where 17 polycyclic aromatic hydrocarbons were found in

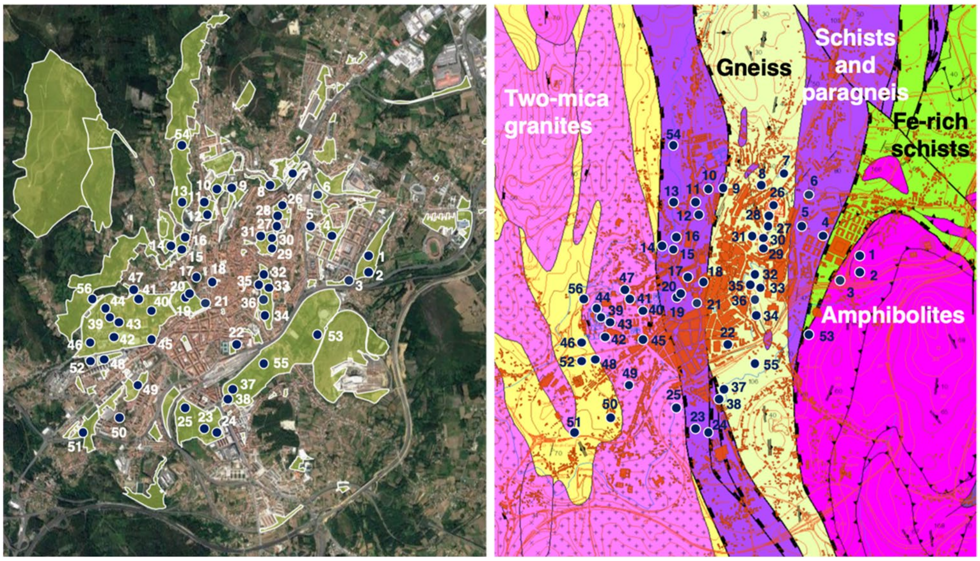

Fig. 1 Sampling points and lithological information of Santiago de Compostela

a widely variable concentration in the soils (between 4 and 4728 ng g^{-1}), being benzo (a) pyrene the compound with the highest risk. Overall, none of the soils analyzed would be considered as contaminated according to the Spanish regulation (Xunta de Galicia 2009).

In the present work, we assessed the mobility and availability of the five trace elements using three chemical extractants. For the determination of soluble, immediately available trace elements, 2 g of air-dry soil (<2 mm) were extracted with 20 mL of 0.01 N $CaCl_2$, shaken for 3 h, and filtered following the method described by Novozamsky et al. (1993). For the assessment of elements available for plant uptake, we followed the method reported by Lakanen and Erviö (1971), weighing 5 g of dry soil, to which 50 mL of $AcONH_4$ 0,5 M, AcOH 0,5 M and Na_2-EDTA extractant solution at pH 4.65 was added, stirring for 1 h. Once the extraction was complete the supernatants were filtered using Whatman grade 40 filter paper. Lastly, bioaccessible elements were determined following the EPA Method 1340 (USEPA 1996), which consists of an extraction of 1 g of soil with 100 mL of a 0.4 M glycine solution at pH 1.5 into a Rotabit incubation chamber (P. Selecta, Barcelona, Spain) at a constant temperature (37±2 °C), with agitation at 30±2 rpm for 1 h. After that time, the soil suspensions were allowed to settle for a few minutes and passed through a 0.45 µm cellulose acetate disk filter.

Trace element concentrations in all the extracts were measured by Inductively Coupled Plasma-Optical Emission Spectroscopy (Perkim Elmer, Optima 4300 DV ICP-OES). All analyses were performed in triplicate.

2.3 Statistics

We used ANOVA mixed model analysis to determine the influence of parent material and land use on the trace metal content of the soils. Previously, the normality of data was checked using the Shapiro-Wilk test. Data that did not pass the normality test were log-transformed for ANOVA. The homogeneity of variance was tested using the Levene test. When a significant effect of land use or lithology at a level of significance of 0.05 was found, the Tukey's multiple range test was used to separate groups. Pearson's correlation analysis between all the soil properties analyzed were also conducted. All statistical analyses were performed using the R statistical package for Windows version R 4.4.2 (R Core Team 2024).

3 Results

3.1 Elements extractable in $CaCl_2$

Table 1 summarizes the results of soluble trace metals (individual results for each soil are shown in the Supplementary information, Table S1). In general, the concentrations followed a decreasing trend Zn>Pb>Ni>Cu>Cr. Only Zn was extracted to relevant extent, whereas Cr concentrations were below the detection limit in all cases (detection limits: 0.003 mg kg^{-1} for Cu and Pb, 0.02 mg kg^{-1} for Ni, 0.03 mg kg^{-1} for Cr, and 0.05 mg kg^{-1} for Zn). The maximum concentration for Zn was 10.6 mg kg^{-1}, always below 2% of the total content of the element. For the other elements, the maximum concentrations were very low: 1.7 mg kg^{-1} for Pb, 0.23 mg kg^{-1} for Ni and 0.17 mg kg^{-1} for Cu, which always represented percentages lower than 1% of the total content. We did not observe significant effect of land use or lithology of the parent material on the concentration of any soluble metal (Fig. 2).

Table 2 shows the Pearson correlations between the soluble fraction of trace metals with each other and with several edaphic properties. As shown in this table, Zn, Cu and Ni presented positive significant correlations among them, and

Table 1 Soluble element concentrations and percentage to total contents. Soluble Cr was not detected in any sample

	Pb		Cu		Zn		Ni	
	mg kg^{-1}	% total	mg kg^{-1}	% total	mg kg^{-1}	% total	mg kg^{-1}	% total
Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Maximum	1.67	0.58	0.17	0.24	10.60	2.19	0.23	0.74
Median	0.00	0.00	0.00	0.00	0.27	0.27	0.03	0.11
Mean	0.05	0.03	0.02	0.02	0.65	0.47	0.04	0.17
Standard deviation	0.23	0.09	0.03	0.04	1.46	0.52	0.04	0.18
ANOVA								
Land use - F	0.4	1.3	1.1	1.3	0.9	1.1	1.2	1.8
p	0.6	0.3	0.3	0.3	0.4	0.3	0.3	0.2
Lithology - F	0.4	0.6	1.8	1.4	1.2	1.4	0.7	1.3
p	0.8	0.7	0.1	0.3	0.3	0.2	0.6	0.3
Land use x Lithology - F	0.2	0.1	0.7	0.5	0.2	0.2	0.3	0.2
p	1.0	1.0	0.7	0.8	1.0	1.0	1.0	1.0

Significance of the effect of land use and lithology is indicated as follows: *significant at a *p*-value of 0.05; **significant at a *p*-value of 0.01; ***significant at a *p*-value of 0.001

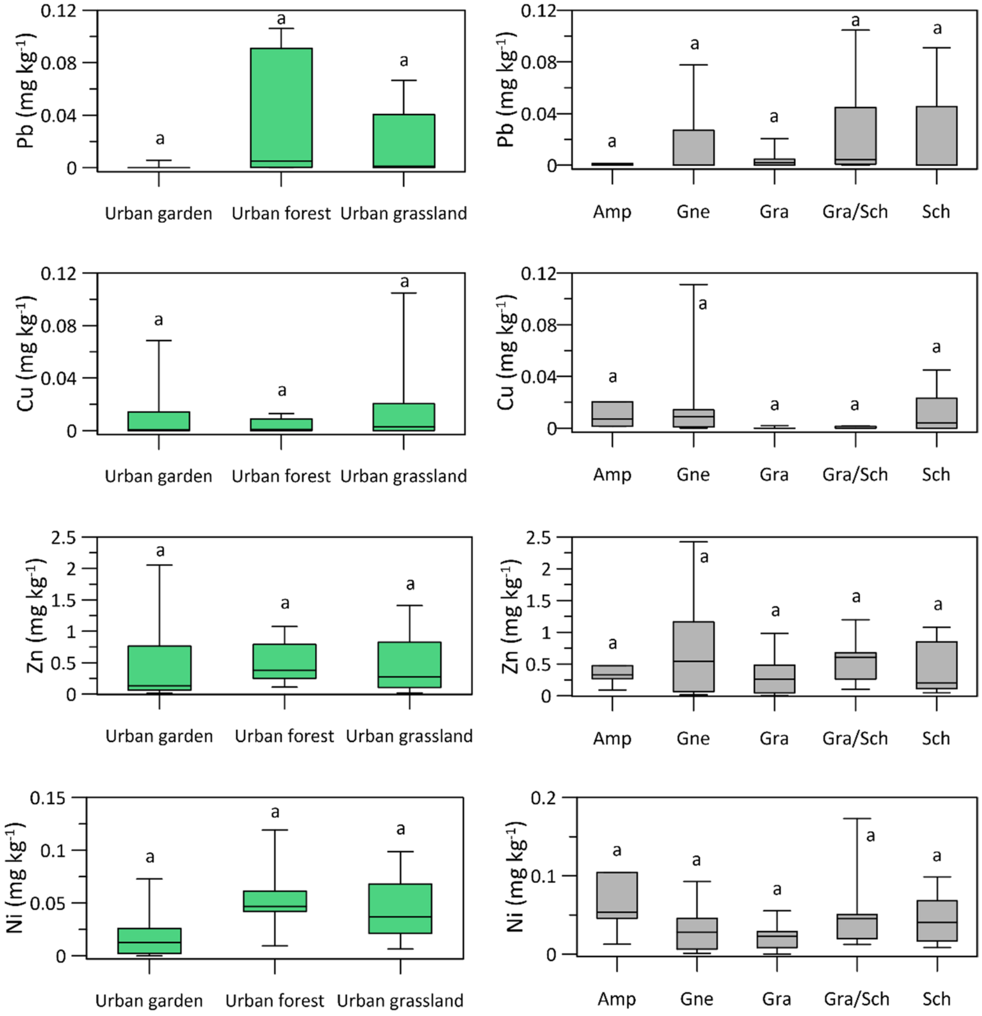

Fig. 2 Soluble elements split by land use and lithology. Different letters mean statistically significant differences between land use or lithology in the Tukey test at *p*-value < 0.05. Amp = amphibolite, Gne = gneiss, Gra = granite, Gra/Sch = Granite/Schist, Sch = schist

Table 2 Pearson's correlation matrix for soluble elements

	pHw	Clay	OC	CEC	Fe_{ox}	Fe_p	Fe_{DCB}	Pb	Cu	Zn
Pb	−0.23	−0.14	−0.05	−0.17	−0.08	−0.02	−0.12	1		
Cu	−0.07	−0.07	−0.09	−0.08	0.03	0.04	−0.11	0.41^{**}	1	
Zn	−0.02	−0.01	−0.02	0.004	0.12	0.13	−0.03	0.07	0.52^{***}	1
Ni	-0.34^{**}	0.15	0.14	−0.17	0.21	0.23	0.13	0.16	0.51^{***}	0.72^{***}

Significance of correlation is indicated as follows: *significant at a *p*-value of 0.05; **significant at a p-value of 0.01; ***significant at a *p*-value of 0.001

Pb was also positively correlated to Cu. Nevertheless, the correlations between trace metals content and edaphic properties were not significant, except for Ni, which was negatively correlated to soil pH. Regarding correlations between soluble forms of the trace metals and their total contents, Pb, Cu and Zn showed significant correlations (Supplementary information, Tables S4-S6), while soluble Ni did not present a significant correlation with Ni total content (Supplementary information, Table S7).

3.2 Elements extractable in EDTA

Table 3 summarizes the results of the EDTA extractions (individual results for each soil are shown in the Supplementary information, Table S2). The average concentrations for all the soils followed a decreasing sequence: Pb > Cu > Zn > Ni > Cr. The element with the highest bioavailability was Pb, with heterogeneous values among soil samples, which ranged between 1.6 and 182 mg kg^{-1}, and

Table 3 Plant-available elements

	Pb		Cu		Zn		Ni		Cr	
	mg kg^{-1}	% total	mg kg^{-1}	% total	mg kg^{-1}	% total	mg kg^{-1}	% total	mg kg^{-1}	% total
Minimum	1.6	4.7	0.3	1.9	0.2	0.3	0.1	0.6	0.0004	0.002
Maximum	182	60	54	36	105	23	3.0	9.3	0.34	0.80
Mean	26	23	10	14	9.4	6.1	0.8	2.9	0.08	0.13
Median	18	23	5.8	12	4.7	4.7	0.6	2.5	0.05	0.15
Standard deviation	34	10	11	8.3	17	4.9	0.6	2.1	0.08	0.08
ANOVA										
Land use - F	1.5	1.2	6.6	5.7	6.1	6.2	1.2	1.5	0.1	0.2
p	0.2	0.3	0.003**	0.005**	0.004**	0.004**	0.3	0.2	0.9	0.8
Lithology - F	1.9	2.1	3.7	6.9	1.8	3.29	1.2	2.4	1.3	1.6
p	0.1	0.1	0.01*	<0.001***	0.1	0.02*	0.3	0.06	0.3	0.2
Land use x Lithology - F	0.2	0.4	0.8	0.5	0.5	0.5	0.4	0.4	0.5	0.2
p	1.0	0.9	0.6	0.8	0.8	0.9	0.9	0.9	0.8	1.0

Significance of the effect of land use and lithology is indicated as follows: *significant at a -value of 0.05; **significant at a *p*-value of 0.01; ***significant at a *p*-value of 0.001

an average value of 26 mg kg^{-1}. In the sequence, Pb was followed by Cu and Zn, whose values ranged between 0.3 and 54 mg kg^{-1} (average of 10 mg kg^{-1}) and between 0.2 and 105 mg kg^{-1} (average of 9.4 mg kg^{-1}), respectively. On the contrary, Ni and Cr were the elements that showed the lowest bioavailability. Bioavailable Ni concentrations ranged between 0.1 and 3.0 mg kg^{-1}, while bioavailable Cr values were practically zero, with a maximum of 0.34 mg kg^{-1}.

In relation to land use, significant differences were observed on bioavailable Cu and Zn concentrations, higher in urban agriculture soils. Concentrations of bioavailable Pb, Ni and Cr did not show significant differences in relation to land use. Regarding lithological influence, significant differences were observed for bioavailable Cu concentration, with lower concentrations on soils developed on granite (Fig. 3).

Table 4 shows the correlations between the plant-available fraction of metals with each other and with various soil properties. Positive correlations were observed between extractable Pb, Cu, Zn and Ni. It is also worth noting the significant correlation of extractable and total Pb, Cu and Zn concentrations (Supplementary information, Tables S4-S6), whereas extractable Ni and Cr showed no significant correlation with their respective total contents (Supplementary information, Tables S7, S8). Regarding edaphic properties, soil pH was positively correlated to available Cu and negatively correlated to Cr. There was a positive correlation between available Zn and Fe_p, as well as between available Ni and clay content, organic carbon, CEC, Fe_{ox} and Fe_p. Available Cr was also positively correlated to organic carbon, CEC, Fe_{ox} and Fe_p.

3.3 Bioaccessibility

Table 5 summarizes the results of the bioaccessibility assessment (results for each individual sample are given in the Supplementary information, Table S3). The mean values for each metal followed a decreasing trend Pb > Cu > Zn > Ni > Cr, with bioaccessible Pb concentrations ranging between 5.5 and 412 mg kg^{-1}, and an average of 64 mg kg^{-1}, being the most bioaccessible element reaching 55% of total content. Bioaccessible Cu and Zn ranged between 1.4 and 101 mg kg^{-1} (average of 23 mg kg^{-1}) and between 1.3 and 188 mg kg^{-1} (average of 21 mg kg^{-1}), respectively. The elements with the lowest bioaccessibility were Ni and Cr, with values between 0.8 and 5.8 mg kg^{-1} for Ni, with an average of 2.1 mg kg^{-1}, while the concentrations of bioavailable Cr ranged between 0.3 and 2.9 mg kg^{-1}, with an average value of 1.1 mg kg^{-1}, which represents 2% of its total content.

In relation to land use, bioaccessible Cu and Zn concentrations were significantly higher in urban garden soils than other uses (Fig. 4). Moreover, bioaccessible Cu concentrations were also higher in soils developed from gneiss, and the same was found for bioaccessible Cr concentrations. The other trace metals did not show significant differences in relation to land use or parent material.

Table 6 shows that all bioaccessible elements were positively correlated among them. Regarding edaphic properties, Ni and Cr were positively correlated to organic carbon, CEC, Fe_{ox} and Fe_p. There was also a positively correlation between Ni and clay content, whereas Cu presented a positive correlation with soil pH. Also, bioaccessible Pb, Cu and Zn were positively correlated with their total contents

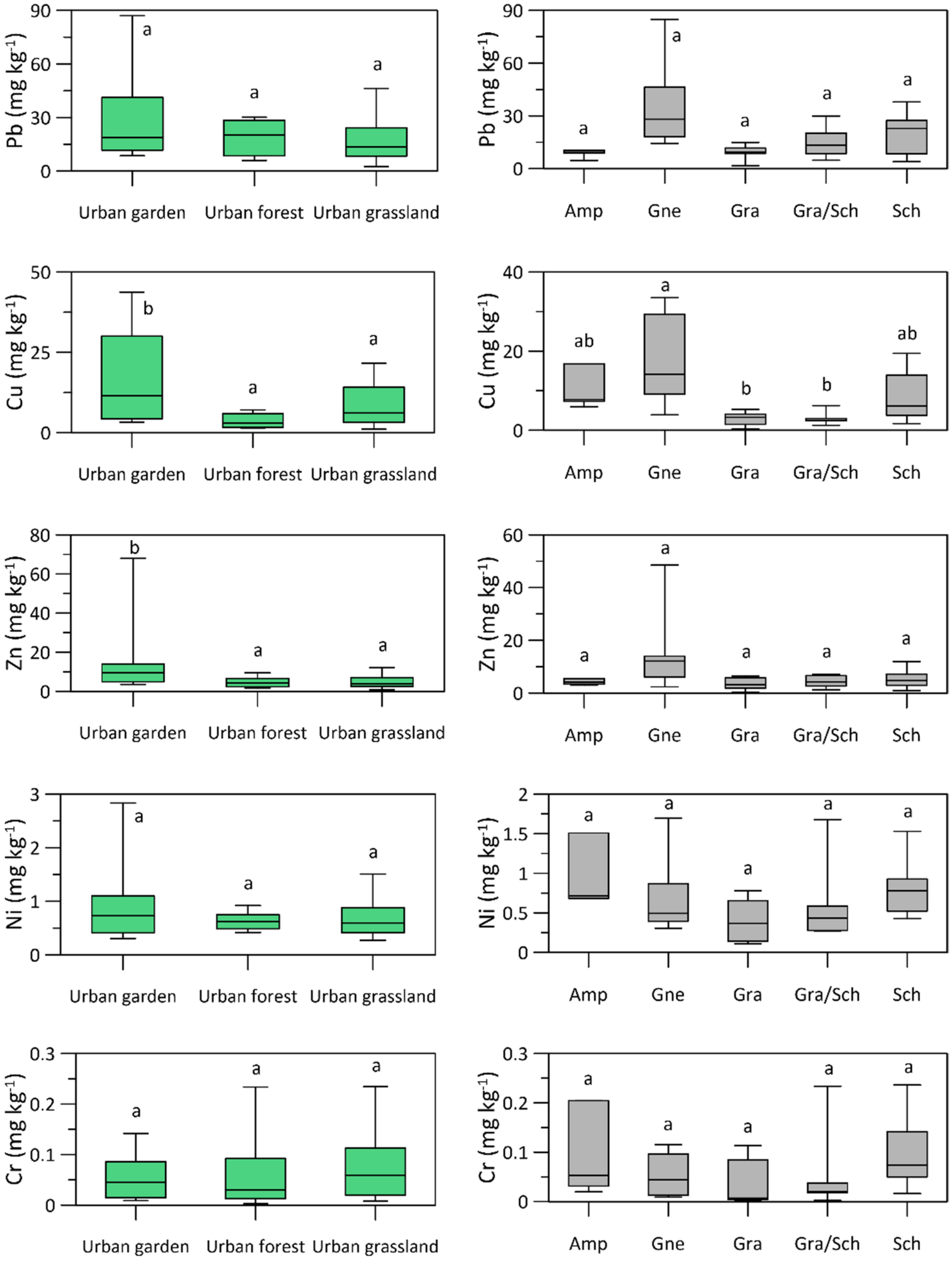

Fig. 3 Plant-available elements split by land use and lithology. Different letters mean statistically significant differences between land use or lithology in the Tukey test at p-value < 0.05. Amp = amphibolite, Gne = gneiss, Gra = granite, Gra/Sch = Granite/Schist, Sch = schist

Table 4 Pearson's correlation matrix for plant-available elements

	pHw	Clay	OC	CEC	Fe_{ox}	Fe_{p}	Fe_{DCB}	Pb	Cu	Zn	Ni
Pb	0.01	−0.05	−0.01	−0.03	0.09	0.25	−0.18	1			
Cu	0.37^{**}	0.13	−0.09	0.10	0.21	0.16	−0.04	0.70^{***}	1		
Zn	0.18	0.07	0.04	0.16	0.16	0.29^{*}	−0.08	0.75^{***}	0.83^{***}	1	
Ni	0.13	0.28^{*}	0.31^{*}	0.39^{**}	0.37^{**}	0.36^{**}	0.15	0.58^{***}	0.75^{***}	0.78^{***}	1
Cr	-0.33^{*}	0.22	0.41^{**}	0.13	0.40^{**}	0.59^{***}	0.15	0.56^{***}	0.23	0.33^{*}	0.43^{**}

Significance of correlation is indicated as follows: *significant at a p-value of 0.05; **significant at a p-value of 0.01; ***significant at a p-value of 0.001

Table 5 Bioaccessible elements

	Pb		Cu		Zn		Ni		Cr	
	mg kg^{-1}	% total	mg kg^{-1}	% total	mg kg^{-1}	% total	mg kg^{-1}	% total	mg kg^{-1}	% total
Minimum	5.5	16	1.4	2.8	1.3	1.9	0.8	2.0	0.3	0.2
Maximum	412	131	101	73	188	57	5.8	19	2.9	6.7
Mean	64	55	23	37	21	14	2.1	8.2	1.1	2.0
Median	41	52	16	39	11	12	1,7	7.3	1.0	1.7
Standard deviation	82	20	21	17	34	11	1.0	4.0	0.5	1.5
ANOVA										
Land use - F	2.3	0.7	4.8	2.0	8.8	12.2	2.6	3.3	3.6	3.9
p	0.1	0.5	0.01^{*}	0.1	$<0.001^{***}$	$<0.001^{***}$	0.1	0.04^{*}	0.03^{*}	0.03^{*}
Lithology - F	2.3	3.6	4.1	5.6	1.9	2.4	1.5	3.3	2.5	9.3
p	0.1	0.01^{*}	0.006^{**}	$<0.001^{***}$	0.1	0.1	0.2	0.01^{*}	0,05	$<0.001^{***}$
Land use x Lithology - F	0.2	0.2	0.6	0.7	0.7	1.1	0.3	1.0	0.7	0.5
p	0.9	1.0	0.8	0.7	0.7	0.4	0.9	0.4	0.7	0.8

Significance of the effect of land use and lithology is indicated as follows: *significant at a *p*-value of 0.05; **significant at a p-value of 0.01; ***significant at a *p*-value of 0.001

(Supplementary information, Tables S4-S6), while this was not found in bioaccessible Ni and Cr (Supplementary information, Tables S7, S8).

4 Discussion

Environmental and health risk related to the presence of pollutants in soils is not only related to their total concentrations, but rather to their mobility and bioavailability, which determine their potential transfer from soil to waters and the food chain. There are several ways to study this risk, among which procedures of chemical extraction are widely employed. The most mobile or effectively bioavailable metals are usually determined by a dilute CaCl$_2$ extraction method by Novozamsky et al. (1993), whereas complexing agents such as ethylene diamine tetraacetic acid (EDTA) or diethylene triamine pentaacetic acid (DTPA) are commonly employed to assess plant availability on the longer term, since they extract exchangeable and OM-complexed elements. Besides, human bioaccessibility can be assessed by in vitro bioaccessibility methods that simulate the stomach digestion to evaluate the amount of trace metals that is available for absorption in human gastrointestinal tissues (Li et al. 2020), including the simplified bioaccessibility extraction test (SBET) described by the US EPA as Method 1340 (USEPA 1996). In this research, we applied the three extraction procedures mentioned above to urban soils, as they provide complementary information about environmental and human health risk. As expected, the amounts extracted were different in each method, following the sequence EPA > EDTA > CaCl$_2$ in most cases, in agreement with what has been observed by other authors in urban and non-urban soils (Luo et al. 2012a; Wang 2014). The metal with the highest solubility was Zn, being the only element with important concentration in the CaCl$_2$ extract, the same found by Crispo et al. (2021) in urban garden soils from the United Kingdom. This fact has been consistently confirmed in the literature in different types of soils, polluted or not (Kabata-Pendias 2010; Cambier et al. 2019), resulting in highest plant uptake of Zn compared to other trace elements (Paradelo et al. 2020). Besides, Zn mobility in these soils is less affected by high SOM contents than other pollutants such as Pb (Paradelo and Barral 2017; Paradelo et al. 2018). Regarding plant availability and bioaccessibility, Pb was the element with the highest concentrations. Similar results were found by Luo et al. (2012a) in Hong Kong city soils and by Zhang et al. (2020) in soils from industrialized areas of China, although the values in Santiago de Compostela were, in general, smaller due to the lower degree of industrialization and anthropogenic pollution in the city.

The sequence and mean percentages found for relative extractability of trace metals were Zn (0.47%) > Ni (0.17%) > Pb (0.03%) > Cu (0.02%) > Ni (below detection limit in all samples). This agrees with other studies where Zn was also the main heavy metal in the CaCl$_2$ extraction (Poggio et al. 2009; Luo et al. 2012a; Wang 2014; Crispo et al. 2021). The very low extractability found is likely related to high organic matter contents in these urban soils (Paradelo et al. 2021), which is common to the soils of the region (Macías and Calvo 2009) such as agricultural soils in Lugo, northwest Spain, where López-Mateo et al. (2023) also reported no environmental risk after CaCl$_2$ extraction, although they found some soil samples exceeding the toxicity threshold for Zn in superficial horizons. All trace elements showed a slightly negative correlation with pH (although only significant for Ni) which is likely related to the well-known decrease of solubility and availability of cationic elements in the soil solution when pH increases (Kabata-Pendias 2010).

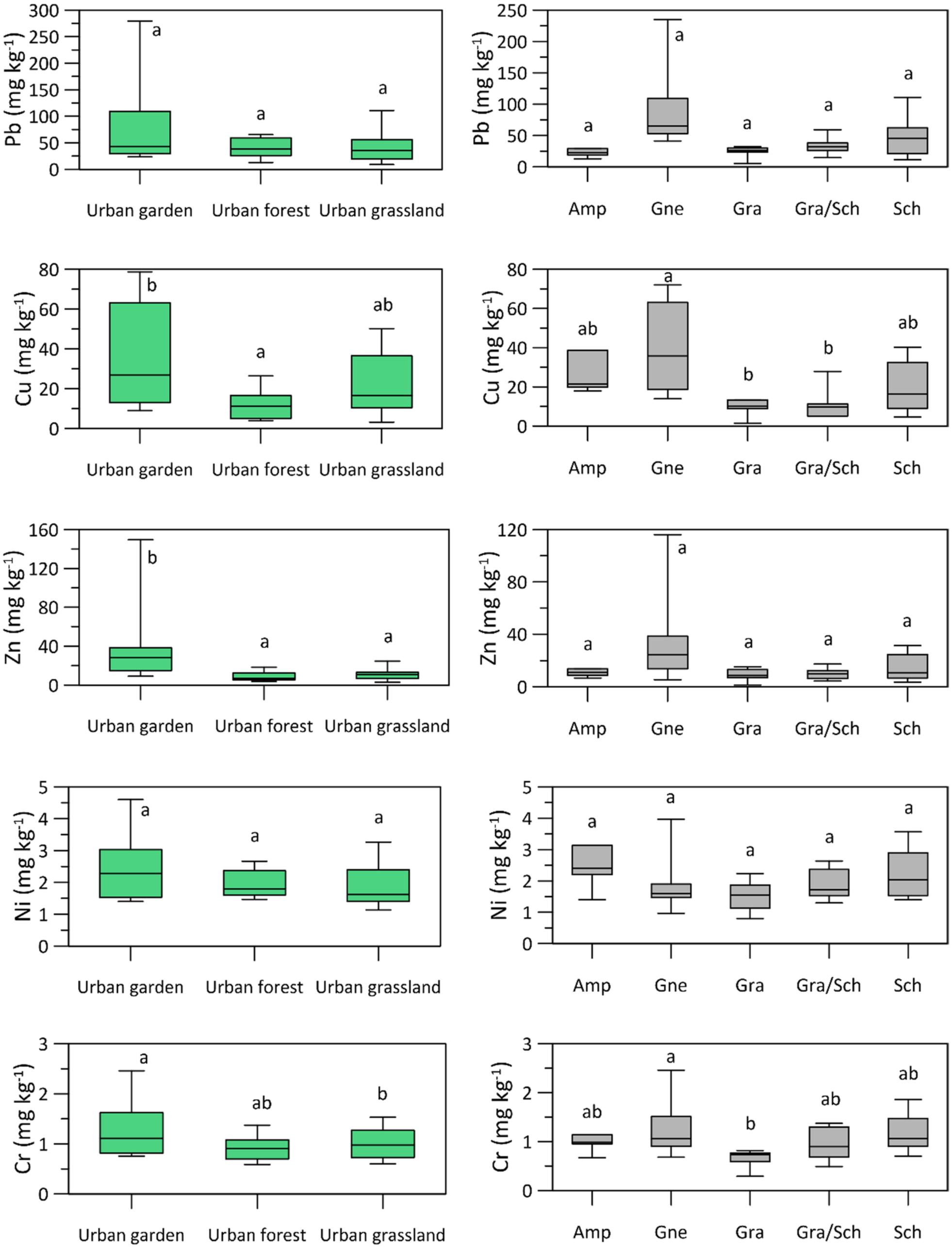

Fig. 4 Bioaccessible elements split by land use and lithology. Different letters mean statistically significant differences between land use or lithology in the Tukey test at *p*-value < 0.05. Amp = amphibolite, Gne = gneiss, Gra = granite, Gra/Sch = Granite/Schist, Sch = schist

Table 6 Pearson's correlation matrix for bioaccessible elements

	pHw	Clay	OC	CEC	Fe_{ox}	Fe_p	Fe_{DCB}	Pb	Cu	Zn	Ni
Pb	0.08	−0.06	−0.07	−0.03	0.07	0.19	−0.20	1			
Cu	0.34*	0.11	−0.14	0.04	0.18	0.10	−0.05	0.76***	1		
Zn	0.26	0.06	0.01	0.17	0,15	0.26	−0.11	0.79***	0.78***	1	
Ni	0.24	0.34*	0.38**	0.51***	0.44***	0.41**	0.19	0.47***	0.57***	0.68***	1
Cr	0.19	0.22	0.29*	0.37**	0.46***	0.58***	0.05	0.69***	0.69***	0.74***	0.71***

Significance of correlation is indicated as follows: *significant at a p-value of 0.05; **significant at a *p*-value of 0.01; ***significant at a *p*-value of 0.001

In the case of EDTA extraction, the sequence and mean percentages were Pb (23%) > Cu (14%) > Zn (6%) > Ni (3%) > Cr (0.1%), the same sequence found by several researches in other European cities such as Athens (Kelepertzis and Argyraki 2015), Turin or Seville (Madrid et al. 2008), as well as in industrial areas in China (Yutong et al. 2016). Nevertheless, the concentrations found in our research were generally lower, corresponding to the lower degree of anthropogenic pollution already mentioned in the soils of Santiago de Compostela (Herbón et al. 2021). The Pearson´s correlation matrix showed significant relationships with clay content, organic carbon and different iron forms for Ni and Cr, which suggests that these metals are closely associated with those soil elements, as found in other studies (Poggio et al. 2009; Cox et al. 2013).

Regarding the range observed in the bioaccessibility values of each element in the urban soils studied, the decreasing sequence and mean percentages of extractability were Pb (55%) > Cu (37%) > Zn (14%) > Ni (8%) > Cr (2%), values overall comparable to those found in previous studies in urban soils from Hong Kong (Luo et al. 2012a), China (Zhu et al. 2015), Bratislava, Slovak Republic (Hiller et al. 2017) and Turin, Italy (Madrid et al. 2008). In contrast, in Xiamen, China (Luo et al. 2012b), in Seville, Spain (Madrid et al. 2008) and in Kumasi, Ghana, (Darko et al. 2017), higher percentages of bioaccessible Zn and Ni were found, in agreement, again, with the lower pollution degree in the urban soils of Santiago de Compostela.

Overall, it was clearly observed that extractability is higher for Pb, Cu and Zn, in comparison to Ni and Cr. In a previous work, we reported that the total concentrations of Pb, Cu and Zn frequently surpassed typical values in non-urban soils, whereas Ni and Cr concentrations were closer to background values for soils over similar parent materials (Herbón et al. 2021). We hypothesized that this observation was due to the fact that Pb, Cu, and Zn reach these soils mostly from anthropogenic sources of pollution, whereas Ni and Cr concentrations were originated from natural sources, this is, the parent material. The results obtained in the extractability studies is consequent with this hypothesis: the very low extractability of Ni and Cr indicates a lithological origin for these elements, probably present in non-extractable mineral forms in the soil geochemical background (Wu et al. 2018; López-Mateo et al. 2023), whereas it is typical that elements that reach the soil from external sources present higher levels of extractability, since they are not natural elements from the background, but derived from anthropogenic activities (Poggio et al. 2009; Szolnoki and Farsang 2013; Valdés Durán et al. 2022), as observed for Pb, Cu and Zn. In any case, this point could be further explored in the future by selective extraction studies.

Urban soils are often used for agricultural activities in urban gardens, which imply a concern about food security, since there may be a risk of vegetable contamination derived from the presence of soil pollutants due to anthropogenic activities in the cities. When we analyzed trace metals mobility in relation to land use, we found significantly higher concentrations of Cu and Zn in urban gardens compared to grasslands and urban forests. These elements were usually employed in many fungicides and insecticides (López-Mateo et al. 2023), which could explain why urban garden soils presented higher concentrations of Cu and Zn in the bioavailable and bioaccessible fractions. However, the risk for human health is, in general, low, since they first need to reach the food chain through plant root uptake, and this seems to not be the case here, since they presented low $CaCl_2$ solubility, likely related to the protective effect of high organic matter content of the soils that, despite acid pH, leads to low mobility among the environmental compartments. The case of Pb is interesting, since it is obviously of anthropogenic origin, and it presented high extractability in EDTA and EPA, but extremely low extractability in $CaCl_2$. This suggests that the risk related to this element in the analyzed soils is also low, since immobilization by soil components, probably organic matter, reduces the amount of soluble element, and thus, the risk of transference to groundwater and living organisms. Nevertheless, as Pb is the element with the highest concentration in the bioaccessible fraction, it could be dangerous for people who accidentally ingest soil, especially for children who spend their free time playing in the ground of gardens and city parks, due to higher hand-to-mouth contacts (Wang et al. 2018). Children can absorb more Pb compared to adults, and this trace metal may have a negative effect in their neurological development (Liu et al. 2018), so adult guidance is critical for children security.

5 Conclusions

The extractability of trace metals in urban soils using three methods for estimation of the soluble fraction ($CaCl_2$ extraction), the bioavailability (EDTA extraction) and the human bioaccessibility (EPA method) led to different results. On the one hand, only Zn was found in soluble forms, in contrast to Pb, Cu, Ni or Cr, whose concentrations were very low, or even under the limit of detection, in the case of Cr. On the other hand, in the extract of exchangeable metals in EDTA and in the in vitro extraction with glycine, the elements with the highest concentration were Pb, Zn and Cu, in that order. Based on this different extractability behavior, the five studied elements could be split in two groups: on the one side, Pb, Zn and Cu, whose concentrations in urban soils are mainly controlled by anthropogenic pollution and, therefore, present higher extractability; and on the other side, Ni and Cr, whose concentrations are mainly related to the parent material and, therefore, present very low extractability. The overall low mobility and extractability observed for all elements are probably related to edaphic properties, such as the high organic matter content typical of the soils of Santiago de Compostela. In this sense, soil management is essential to avoid risks of pollutant transference to the food chain and natural waters, and it seems that practices oriented to conserve and/or increase organic matter levels are the best option to ensure the trace metals adsorption and avoid their release into the soil solution.

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Declarations

Competing interests The authors have no competing interests to declare that are relevant to the content of this article.

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