Health risk assessment via ingestion and inhalation of soil PTE of an urban area

DOI:10.1016/j.chemosphere.2021.130964

Health risk assessment via ingestion and inhalation of soil PTE of an urban area

Li Yan[a*], Ajmone-Marsan Franco[a], Padoan Elio[a]

[a]University of Turin, Department of Agricultural, Forest and Food Sciences, Grugliasco, 10095, Italy

*Corresponding Author: Li Yan

Address: Department of Agricultural, Forest and Food Sciences, University of Turin, Via Largo Paolo Braccini 2, Grugliasco (Torino) 10095, Italy.

E-mail: yan.li@unito.it

Abstract

Potentially Toxic Elements (PTE) are common soil contaminants and pose a significant risk to human health. In this study, ingestion (<150 μm) and inhalation (<10 μm) bioaccessibility and human health risk due to PTE were investigated in soils of the urban and peri-urban area of Torino. Lead, Cd, Cu, and Zn were observed to be the most soluble elements in simulated gastric and lung fluids. Higher bioaccessible concentrations of Pb, Ni, Co and Sb were observed in the inhalable size fraction (< 10 μm) compared to ingestible one probably because of the higher concentration in fine soil size fraction. Conversely, the relative bioaccessibility of Pb, Cu, Cd, Zn and As was lower, due to the different extracting conditions and to the presumable different elemental speciation. Average values suggested that PTE would be more bioavailable if ingested than inhaled, particularly in urban areas, were the bioaccessible percentages were always higher than in peri-urban sites. Health risk assessment was conducted using bioaccessible concentrations and their corresponding toxicities via ingestion and inhalation exposures. Unacceptable non-carcinogenic risk (HQ > 1) was found through ingestion exposure for children in some urban sites and Pb was the most hazardous elements. Carcinogenic risks were under the threshold levels for every soil (CR < 10^{-4}), with Cr and As being the dominant contributors to risk. Therefore, necessary soil remediation activities are needed to reduce the risks of human, especially for children, exposure to Pb.

Keywords: Potentially Toxic Elements, urban area, peri-urban area, oral bioaccessibility, lung bioaccessibility

Highlights:

- Gastric and lung bioaccessibility in diverse soil size fractions were investigated
- PTE would be more bioavailable if ingested than inhaled
- Higher bioaccessibility was visible in urban sites
- Pb was, still, the most important element for non-carcinogenic risk

1. Introduction

Rapid industrialization and expansion of urban areas lead to the entrance of numerous Potentially Toxic Elements (PTE) to soil (Kabata Pendias, 2010; Ajmone-Marsan and Biasioli, 2010). As PTE tend to accumulate in soils, in cities people exposure to contaminated soils can pose significant human health risk, due mainly to the routes connected to oral ingestion and inhalation (Manjon et al., 2020; Marini et al., 2021). In most cases, health risk assessment has been conducted considering PTE total concentrations; however, not all the elemental species are available for adsorption and the use of total or pseudo-total contents may somewhat overestimate the risk, as already reported from many researchers (Paustenbach, 2000; Han et al., 2020; Mokhtarzadeh et al., 2020). In recent years, different *in vitro* methods have been used for estimating the PTE gastrointestinal bioaccessibility, especially the Simple Bioaccessibility Extraction Test (SBET), which has been widely applied for human health risk assessment (Oomen et al., 2002; Li et al., 2020).

To correctly estimate the risk due to ingestion, in addition to the SBET, or similar extraction methods, studies need to analyze the bioaccessibility only on the potentially ingestible fraction of soil (i.e. the fraction of soil <150 μm) (Li et al., 2021).

The second most important route for PTE interaction with urban population is inhalation, which involves the soil fine size fractions (i.e. particles <10 μm), as they are easily resuspended by anthropogenic activities and wind erosion. Thus, PTE in fine particles may easily enter the nasal cavity and lungs through inhalation (Kastury et al., 2018; Li et al., 2020). Until now, no unified analytical protocol for the determination of lung bioaccessibility has been adopted, and this poses many challenges for methodologies comparison (Ren et al., 2020). Recently, a new study (Zhong et al., 2020) obtained a good *in vitro*-*in vivo* correlation using optimized Gamble solution (Wragg and Klinck, 2007). The method showed good performance for the prediction of lung bioaccessible PTE and has been proposed for human exposure assessment.

Turin is the third-largest city in Italy, which has a long industrial history and may represent a model for cities with historical contaminations, as the industrial activities were concentrated in the city centre while the peri-urban area was mostly residential and surrounded by agricultural fields. Previous studies in this area evidenced this difference between the urban and the peri-urban area (Biasioli et al., 2006; Padoan et al., 2017), however few studies were carried out to the bioaccessibility of PTE in the particle size-associated fractions (Padoan et al., 2017; Pelfrêne and Douay, 2018) and to assess the health risk via the combined ingestion and inhalation pathways, essential to determine the exposure risk. Therefore, the objectives of this study are: (1) to investigate the concentration and distribution of PTE in soils of the urban and peri-urban areas; (2) to assess the gastrointestinal and lung bioaccessibility of PTE; (3) to estimate health hazards due to non-carcinogenic and carcinogenic elements via ingestion and inhalation exposure based on bioaccessibility data.

2. Materials and methods

2.1 Study area

The metropolitan area of Turin (45°04′ N; 7°41′ E) lies on an alluvial plain in the Piemonte region, in north-west Italy, and has a population of 1.7 million inhabitants. It features a very large amount of vehicular traffic and has a long history of industry, primarily car-manufacturing factories, and metallurgical industries (Padoan et al., 2017).

Soil sampling sites were selected along a main road across the city, on a South-North directory, beginning and ending in the peri-urban area (Figure 1). Sites in the peri-urban area (n=10) were surrounded by agricultural fields and sites in the urban area sites (n=20) were distributed on roadsides and parks.

2.2 Soil sampling

Samples collection was conducted in January and May 2020, a total of 30 topsoil samples were collected from the study area. Each sample was taken at a 0-10 cm depth and a composite soil sample at each site was obtained by mixing three sub-samples at a distance of 1 m away from each other. The collected samples were put in plastic bags and homogenized. All samples were air dried in laboratory at room temperature and sieved through a 2 mm plastic sieve to remove stones, plant, and anthropic fragments (plastic, glass, metallic, etc.) before further analyses.

2.3 Sample characterization

The pH of soil samples was measured in 1:2.5 soil/water suspensions by using a pH meter with a combined glass electrode, total carbon (TC) and total nitrogen (TN) were measured by an element analyser (CE Instruments, NA2100 Elemental Analyzer, ISO 10694), carbonates were analysed by volumetric method (ISO 10693). Particle size distribution and fraction below 10 μm were measured and collected via the hydrometer method (Padoan et al., 2017). Soil digestion and measurement of pseudo-total PTE were carried out according to Ajmone-Marsan et al. (2019). A portion of each sample was crushed to pass through 0.15 mm sieves, 1.00 g soil sample was weighed and microwave-digested with *aqua regia* (HCl/HNO_3, 3:1 v/v, Milestone Ethos D, ISO 11466)) and then determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer NexION® 350D). All the determinations were carried out in triplicate. Accuracy was checked against a certified reference material for *aqua regia* extractable elements in calcareous soil (CRM 141R).

Along with concentrations in bulk soil (<2 mm), pseudo-total PTE concentrations were analysed in the <10 μm and in the <150 μm fraction using the same procedure.

2.4 *In vitro* gastric and lung bioaccessibility

The gastric bioaccessibility of the elements was determined using the SBET method (Ruby et al., 1999; Oomen et al., 2002). In brief, soil samples sieved at 0.15 mm were used; 0.5 g of sample was weighed and mixed with 50 mL of a 0.4 M glycine solution with pH adjusted to 1.5 by concentrated HCl. The mixture was shaken at 150 rpm, incubated at 37°C for 1 h and then centrifuged at 3000 rpm for 10 minutes, the supernatant was taken and filtered through a 0.45 µm cellulose filter prior to the analysis.

The lung bioaccessibility test was performed using the optimized Gamble Solution (the chemical composition of the solution presented in Table S1). Briefly, <10 µm soil samples were weighed accurately into labelled 50 mL tubes and mixed with solution at a solid:solution ratio of 1:1000; the mixture was then shaken at 37°C for 24h. After oscillation, the extracts were centrifuged at 3000 rpm for 10 minutes; the supernatant was taken and filtered through a 0.45 µm cellulose filter. All extraction solutions were freshly prepared, and all the determinations were carried out in triplicate, the extractant was analysed by ICP-MS.

The bioaccessibility was calculated as follows (Du et al., 2020):

$$\text{Bioaccessibility (\%)} = (C_{\text{in vitro}}/C_{\text{total}}) \times 100$$

Where $C_{\text{in vitro}}$ is the bioaccessible concentration of PTE as determined using the *in vitro* extraction, and C_{total} is the *aqua regia* concentration in the considered soil fraction.

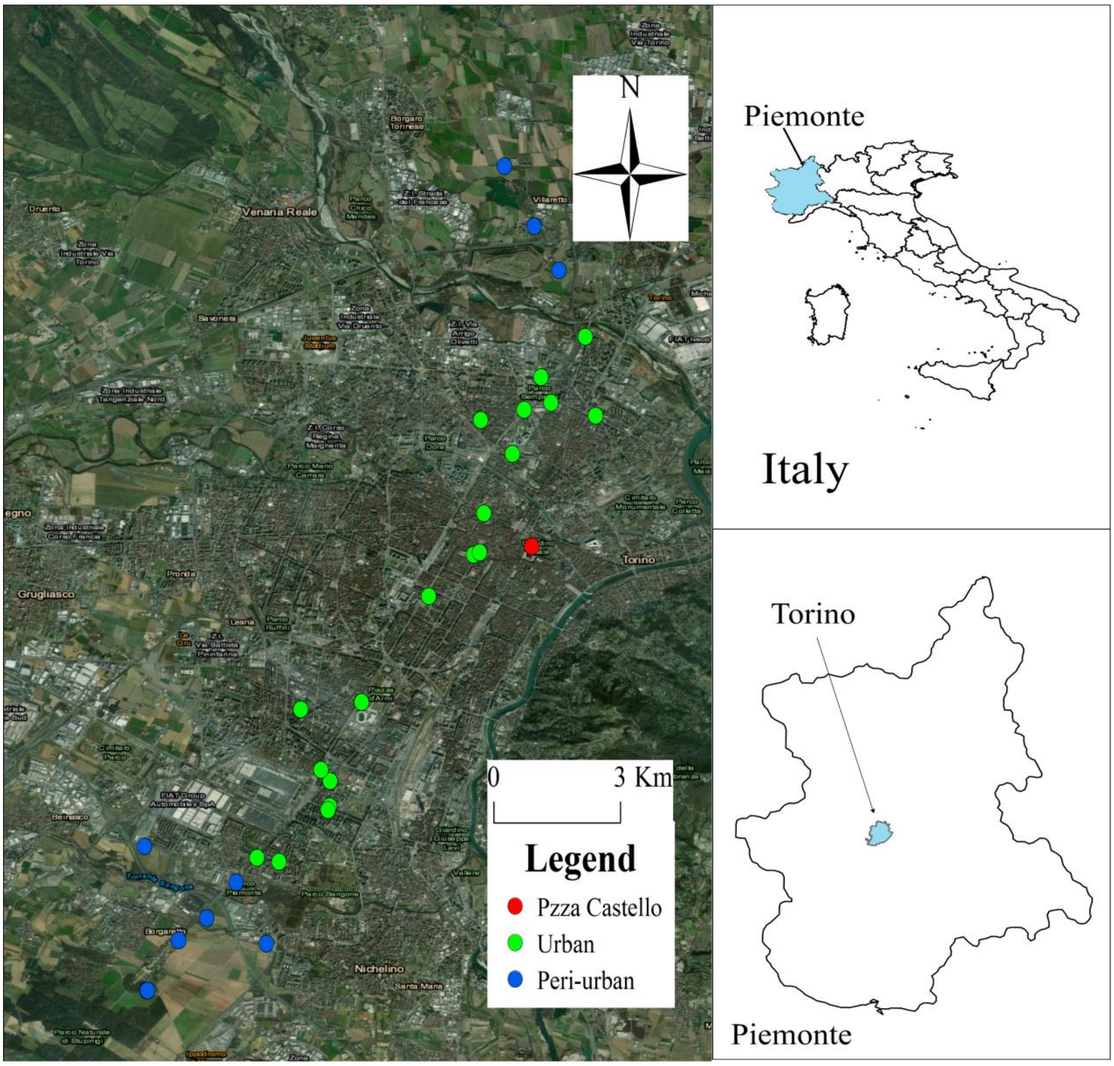


Figure 1. Sampling sites and map of the study area in Turin, Italy.

2.5 Human health risk assessment

The non-carcinogenic risk (hazard quotients; HQ) and carcinogenic risk (CR) which proposed by US Environmental Protection Agency (USEPA, 2004) have been widely used to quantify the risk of people exposure to PTE contaminated soil. Exposure of humans to PTE in soils can be categorized into three pathways: inadvertent oral ingestion, dermal contact, and inhalation (Paustenbach, 2000). Based on the guidelines and Exposure Factors Handbook (USEPA, 1989, 1997, 2002), chemical daily intake (ADD, mg/kg/day) of PTE through different pathways from soil were calculated using the following equations (1) - (2).

$$ADD_{ing} = C_{(Gastric)} \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (1)$$

$$ADD_{inh} = C_{(Pulmonary)} \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (2)$$

Where ADD_{ing}, ADD_{inh} are the daily amount of elemental intake via ingestion and inhalation. $C_{(Gastric)}$ and $C_{(Pulmonary)}$ are the bioaccessible concentration (mg/kg) in simulated gastric and lung fluids. Other parameters are given in Table 1.

The hazard quotients (HQ, Eq. (3)) and the hazard index (HI, Eq. (4)) were used to characterize the non-carcinogenic hazard.

$$HQ_i = \frac{ADD_i}{RfD_i} \quad (3)$$

$$HI = \sum HQ_i = \sum \frac{ADD_i}{RfD_i} \quad (4)$$

Where RfDi is the reference does of the specific element (mg/kg/day). When HQ or HI < 1, it indicates that no potential non-carcinogenic risk for humans, and HQ > 1 or HI >1 indicates adverse health effects (USEPA, 2011).

Carcinogenic risk (CR) was calculated using the dose of PTE multiply the corresponding slope factor (Eq. (5)) and it was assumed that all the element risks were additive (Li et al., 2012; Luo et al., 2012).

$$CR = ADD_i \times SF_i \quad (5)$$

$$TCR = \sum CR \quad (6)$$

Where SF is the slope factor of carcinogenicity (mg/kg/day). When $10^{-6} < CR < 10^{-4}$ is considered acceptable (USEPA, 2011), while $CR > 10^{-4}$ means a carcinogenic risk to human health (Li et al., 2014; Guney et al., 2010; USEPA, 1989). The values of RfD and SF for different PTE are shown in Table 2.

Table 1. Definition and reference value of some parameters for health risk assessment of PTE in soils.

Parameters	Definition	Units	Values		Reference
			Adult	Child	
IngR	Soil ingestion rate	mg/day	100	200	US DOE (2011)

EF	Exposure frequency	day/year	350	350	US EPA (2002)
ED	Exposure duration	year	24	6	US DOE (2011)
BW	Body weight	kg	70	15	US EPA (2002)
AT	Average time	day	365×ED (non-carcinogen)/ /365×70 (carcinogen)		US EPA (2002)
InhR	Soil inhalation rate	m^3/day	20	7.5	US DOE (2011)
PEF	Soil to air particulate emission factor	m^3/kg	1.36×10^9	1.36×10^9	US EPA (2002)

Table 2. Summary of reference does (RfD) and slope factor (SF) of different PTE.

Metals	RfD (mg/kg/day)		SF (mg/kg•day)	
	Ingestion	Inhalation	Ingestion	Inhalation
Cd	$1.0\cdot10^{-03}$	$1.0\cdot10^{-02}$		6.3
Cr	$3.0\cdot10^{-03}$[a]	$2.86\cdot10^{-05}$	$5.01\cdot10^{-01}$	$4.2\cdot10^{-01}$
Ni	$2.0\cdot10^{-02}$	$2.0\cdot10^{-02}$		
Zn	$3.0\cdot10^{-01}$	$3.0\cdot10^{-01}$		
Cu	$4.0\cdot10^{-02}$	$4.0\cdot10^{-02}$		
Pb	$3.5\cdot10^{-03}$[b]	$3.5\cdot10^{-02}$	$8.5\cdot10^{-03}$	$4.2\cdot10^{-02}$[c]
As	$3.0\cdot10^{-02}$	$3.0\cdot10^{-03}$	1.5	$4.3\cdot10^{-03}$
References	USDOE, 2011	USDOE, 2011	Adimalla, 2020	Adimalla, 2020

a USEPA (2002)
b WHO (1993)
c Wang et al. (2020)

2.5 Statistical analysis

Data processing and statistical analysis were conducted with Microsoft Excel 2010 and Origin 8.0.

3. Results and discussion

3.1 Physicochemical properties of soils

In Table 3, the mean values of the soil physicochemical properties in the urban and peri-urban area are presented. Soils pH in the peri-urban area (agricultural soils) were slightly acidic, however, urban soils were neutral to alkaline, consistently with previous studies highlighting this difference, which may be due to the historical inclusion of extraneous materials (Biasioli et al., 2006). The sand content (50 µm - 2 mm) was almost constant in all samples, with a mean value of 65%. Total carbon (TC) and carbonates content in the urban area were, on average, higher than in peri-urban areas, with carbonate content in line with differences in pH. The higher TC was probably due to the sampling areas, as most of the urban area soils were covered by grass or trees, with a possible variable but low contribution from exogenous organic pollutants such as hydrocarbons or plastics.

The descriptive statistics summary of PTE concentrations in samples is presented in Table 4. The mean and median concentrations of all the elements (except As) were higher in the urban area than in peri-urban locations. The concentration of all the elements were higher than the average values of European and world soils (Kabata-Pendias 2010) in both peri-urban and urban areas. Compared to a previous study (Padoan et al., 2017), peri-urban concentrations were lower, while some elements in urban area, such as Cd and Ni, were a little higher.

Little can be said about the spatial trends within the city, as the variability of the distribution of PTE within an urban area is exceedingly high (Ajmone and Biasioli 2010).

Considering only the transect, PTE presented a higher pollution degree in the middle of the city, near the historical centre, and lower concentrations at the edge of the city, in the peri-urban area (Figure S1). High concentration of Ni was documented in a roadside park, while Cr presented no obvious polluting sources, confirming that Cr and Ni concentrations in soils were primarily controlled by parent materials (Ajmone-Marsan et al., 2008).

Copper and Zn had similar spatial distributions, indicating that they may originate from the same source. The highest concentrations were found in the central and northern part of the city, coherently with previous studies indicating Cu and Zn as mainly originating from vehicle factories and traffic (Grigoratos and Martini, 2015). Two Pb hotspots were located in the north of the study area, near two gas stations, and in trafficked sites; thus, the high concentrations may derive from fuel leakage or diffuse contamination. Antimony, also, was concentrated in the northern part of the city, which is the oldest industrialized area (Figure S2).

These few hints, together with the results of previous studies (Biasioli et al., 2006), suggest the use of distance patterns (e.g. from the city centre) in place of a systematic sampling to evaluate the effects of a city on the transportation and disposal of pollutants within its boundaries giving the heterogeneity of human activities contribution to the content of PTE in urban soils.

Table 3. Descriptive statistics of the peri-urban and urban area soil properties.

	pH	TN	TC	Carbonates	Particle size distribution (mass %)				
		%	%	%	< 2 μm	2-20 μm	20-50 μm	50-200 μm	> 200 μm
					Peri-urban area				
Mean	6.53	0.35	3.10	0.76	4.3	19.2	13.2	43.5	19.9
Median	6.27	0.39	3.41	0.65	3.9	19.8	13.5	45.4	21.0
Max	8.00	0.59	5.39	1.77	7.9	26.5	16.8	51.7	31.5
Min	5.70	0.10	0.75	0.33	1.2	11.7	8.9	32.2	7.9
Std.Dev	0.72	0.17	1.54	0.39	2.3	4.7	2.3	5.5	7.3
					Urban Area				
Mean	7.42	0.37	4.02	1.05	4.8	18.3	12.1	34.5	30.3
Median	7.46	0.34	3.56	1.01	4.7	17.8	12.0	31.4	28.6
Max	7.91	0.64	6.36	2.29	8.9	27.8	20.8	58.9	54.9
Min	6.53	0.21	2.16	0.32	0.2	5.7	7.5	21.5	17.5
Std.Dev	0.31	0.12	1.44	0.58	2.0	6.5	3.2	9.9	11.2

Table 4. Summary statistics of PTE (mg/kg) in the peri-urban and urban area. (significant differences ($p < 0.05$) between the two areas are represented from different lower-case letters in the same column).

	Cr	Ni	Cu	Zn	Pb	Co	Cd	Sb	As
Peri-urban area									
Mean	265	**187 b**	**47 b**	**145 b**	**66 b**	20	1.0	**1.2 b**	7.9

Median	206	162	43	130	54	20	0.6	1.0	7.7
Max	461	289	94	322	196	25	4.6	2.5	12.1
Min	158	125	26	72	24	14	0.4	0.7	5.3
Std.Dev	121	56	19	66	48	3.5	1.3	0.5	1.7
Urban area									
Mean	270	**240 a**	**90 a**	**216 a**	**220 a**	23	1.3	**4.1 a**	7.5
Median	236	222	69	167	86	22	0.6	2.8	6.8
Max	665	632	257	551	1174	37	7.9	19.1	11.7
Min	117	104	31	89	27	15	0.3	0.9	0.7
Std.Dev	128	113	56	139	319	5	1.7	4.1	2.8
Previous study[1]	405	254	128	286	319		0.6	5.4	
European soils[2]	59.5	37	38.9	68.1	32				11.6
Worldwide soils[2]	94.8	29	17.3	70	27	10			6.8
Legislative limit[3]	150	120	120	150	100 ab	11	2	10	

[1] Padoan et al., 2017

[2] Kabata-Pendias, 2010

[3] Metha et al., 2020

3.2 *In vitro* bioaccessibility of PTE in urban and peri-urban areas

3.2.1 Oral bioaccessibility

Bioaccessible percentages and relative concentrations for the studied PTE are presented in Figure 2 and Table 5 for the urban and peri-urban areas. The data showed that the bioaccessibility of Pb, Zn and Co ($p < 0.05$) in the urban area was significantly higher than in the peri-urban area, although all the elements were more bioaccessible in the urban area. The bioaccessibility trend between elements was similar in both areas; i.e. Pb > Cd, Cu > Zn > Co > As, Ni, Sb > Cr. Moderate to weak correlations between total concentrations and bioaccessibility were observed for Cu (R^2=0.67), Zn (R^2=0.54), Pb (R^2=0.43), and Ni (R^2=0.33), while there was no clear connection in the case of Cr and Cd (R^2<0.10, Fig. S3). These observations corroborated previous studies where PTE bioaccessibility in soils varied significantly between sampling sites and elements (Wu et al., 2017; Ai et al., 2019). Many factors contribute to the disparity in bioaccessibility values, which one of the most important is the presence of different sources of elements (Kelepertzis, 2014; Liu et al., 2019) whose possibly include diverse fractions of PTE with different bioaccessibilities (Liu et al., 2019). High bioaccessibility of Pb, Zn, and Cu has been linked to a higher level of anthropogenic pollution (Liu et al., 2017; Padoan et al., 2017), since elements from anthropogenic sources are generally more soluble in the gastrointestinal environment and thereby more bioaccessible (Luo et al., 2019; Hernandez-Pellon et al., 2018). Huang et al. (2018) also reported that PTE originated in a residential area were more bioaccessible than ones originated in commercial and industrial areas. Furthermore, the PTE speciation need to be considered; the low bioaccessibility of Cr, for example, may be due to the high geogenic contribution of refractory chromium-containing minerals from serpentinites, which cannot be easily solubilized (Sialelli et al., 2011; Biasioli et al., 2006). A very high bioaccessibility of Cd was observed during *in vitro* digestion, as found also in different areas (Luo et al., 2012; Francova et al., 2020) and the results may be associated with the low pH in simulated extraction solutions (Li et al., 2016).

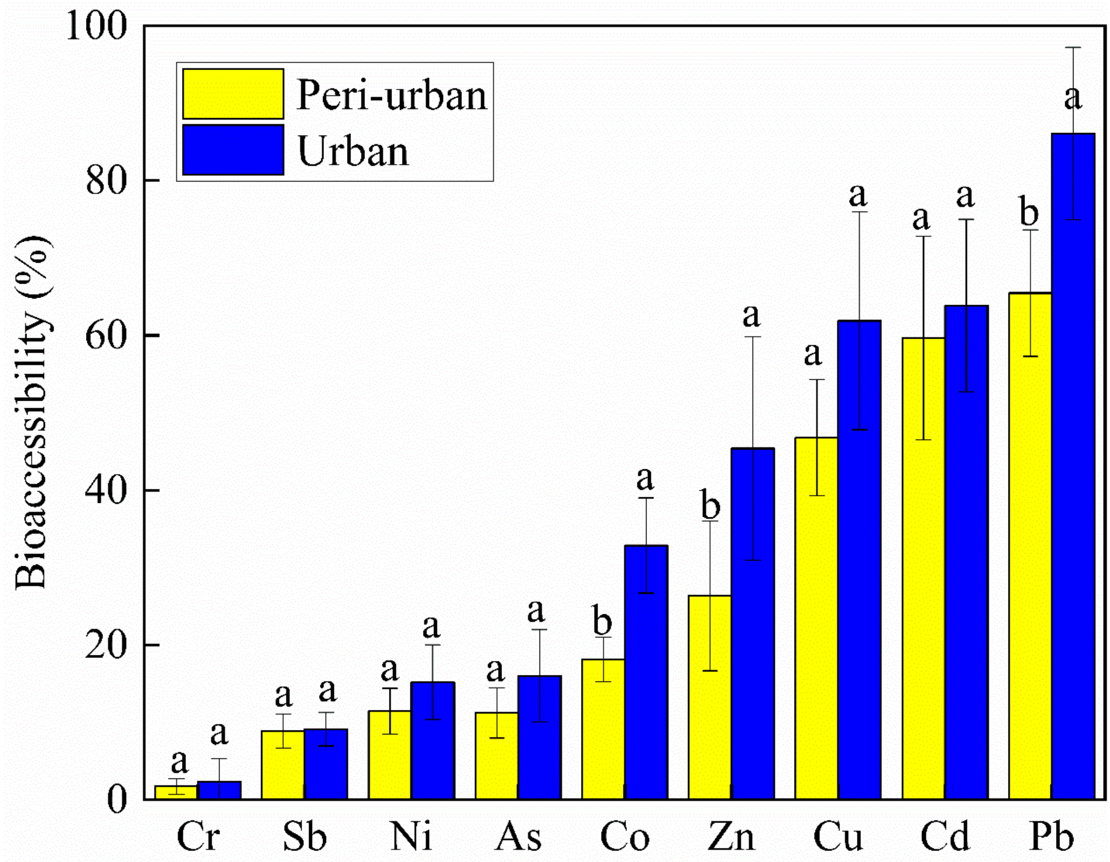


Figure 2.Gastric bioaccessibility of PTE in the urban and peri-urban area. Lower-case letters show significant difference ($p < 0.05$) of different element bioaccessibility between areas.

3.2.2 Lung bioaccessibility

Elements associated with fine soil size fraction (<10 µm) may pose potential health risks because they can directly enter into the lung then to the blood system via inhalation. The results of the total and bioaccessible concentrations, and inhalation bioaccessibility in soils (<10 µm) were displayed in Table 5 and Figure 3. Bioaccessible PTE concentrations (Co, Ni, Sb and Pb) through inhalation were higher than ones through ingestion ($p < 0.05$), posing concerns to their possible harm. However, the relative bioaccessibility was lower (Fig. 4) because of the high total concentrations in the <10 µm fraction, higher than in coarser fractions. The higher concentrations has already been reported from many articles and is due to different phenomenon, such as, in some case, to the increase of sorption due to the higher specific surface of fine particles, according to what was already been reported (Ajmone-Marsan et al., 2008; Ma et al., 2019).

The differences in bioaccessibility may be due also to the different components of the extracting solutions and to pH values of the *in vitro* methods (Hu et al., 2019; Monneron et al., 2020). Many researchers found that pH has a substantial impact on PTE bioaccessibility (Liu et al., 2018). In opposition with these results, PTE bioaccessibility generally decrease with a higher pH (Basta et al., 1993; Li et al., 2020), however, the complexity of Gamble's solution could probably have resulted in a different behaviour as, for example, the presence of chlorides in its formula could lead in the formation of metal-chloride complexes which are readily solubilized (Bourliva et al., 2020).

The lung bioaccessibility varied widely among different elements because of the different chemical forms in which the elements could be present in the urban setting. Lead, Cd, Cu, and Co had the highest bioaccessibility, followed by Sb, Zn, As, Ni and Cr. The relatively high bioaccessibility of Cu and Zn may be due to the presence of cysteine in the extraction solution, which provides thiol groups that strongly coordinated with Zn and Cu (Huang et al., 2014). The high bioaccessibility of Cd is also interesting. According to a previous study (Pelfrêne and Douay, 2018), between the major forms of the elements present in the environment, Cd oxide and Cd chloride are easily dissolved in the lung, however, Cd sulfide not.

Lead, Cu, Zn, Ni, and Co had a higher bioaccessibility in the urban than in the peri-urban area, although not statistically significant, while Cr, As, Sb and Cd where more bioaccessible in the peri-urban area. This variability highlighted that PTE release could be influenced by the geological origins and by different anthropogenic processes.

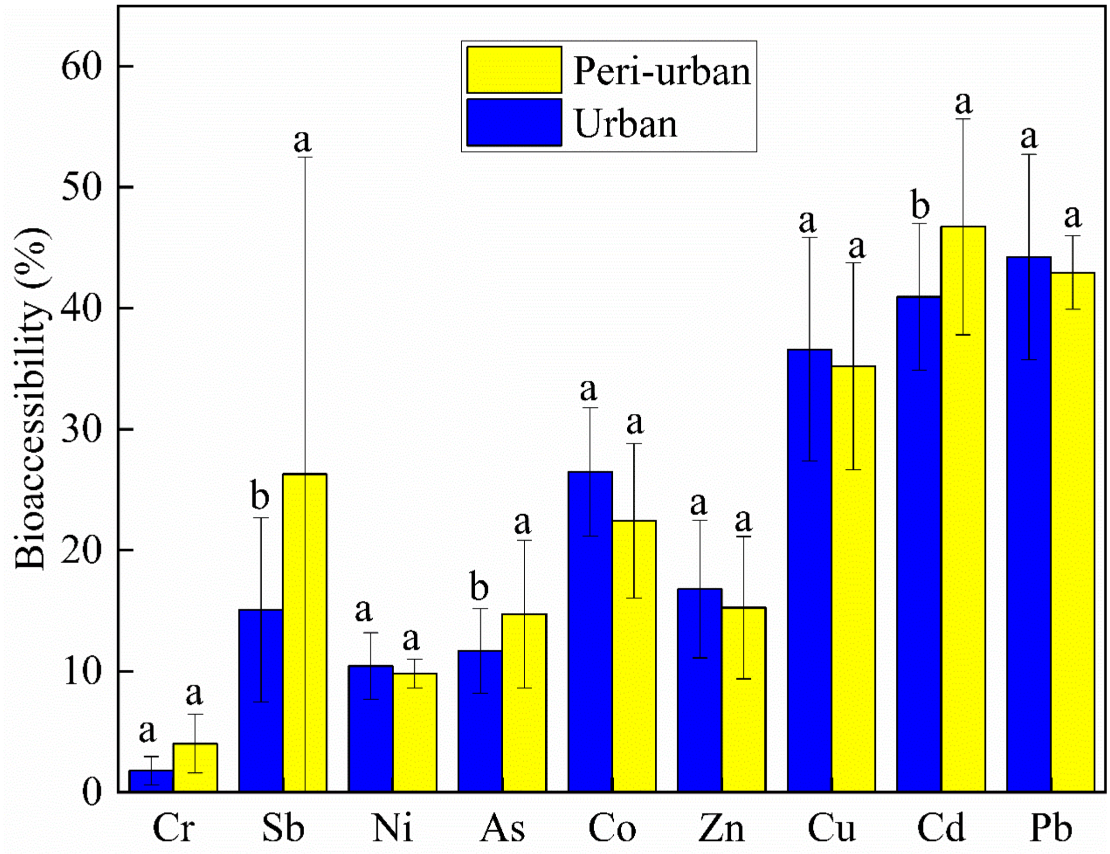


Figure 3. Lung bioaccessibility of PTE in the urban and peri-urban area. Lower-case letters show significant difference ($p < 0.05$) of different element bioaccessibility between areas.

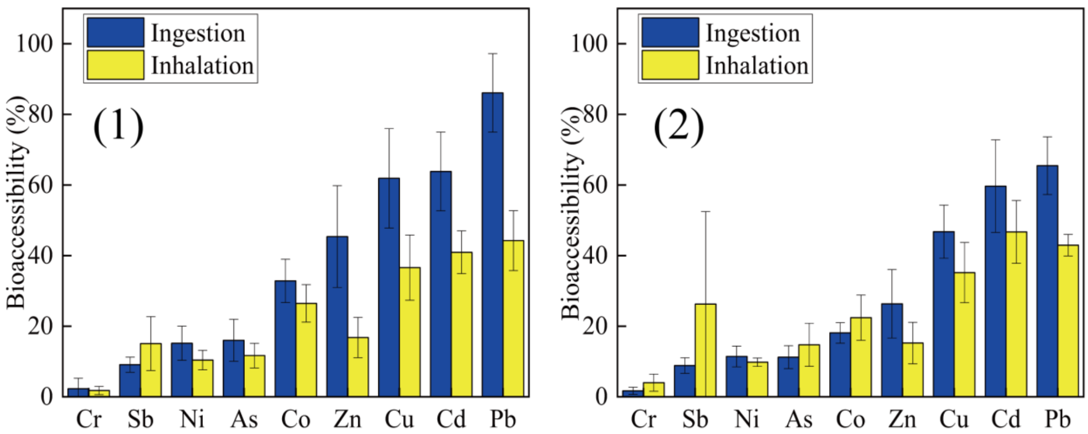


Figure 4. Comparison of PTE oral and lung bioaccessibility in urban (1) and peri-urban (2) area.

Table 5. Total (< 10μm) and bioaccessible (<150 μm, <10μm) PTE concentrations (mg/kg) in the urban and peri-urban area. Ranges, Median (Med), Averages (Avg) and Standard Deviations (SD). Upper-case letters show significant differences ($p < 0.05$) between ingestion

and inhalation in the urban area, while lower-case letters indicate significant differences ($p < 0.05$) in the peri-urban area.

	Total concentration (< 10µm)						Urban Area						Peri-urban Area					
	Urban			Peri-urban			Bioaccessible concentration (< 150 µm)			Bioaccessible concentration (< 10 µm)			Bioaccessible concentration (< 150 µm)			Bioaccessible concentration (< 10 µm)		
	Range	Med	Ave±SD	Range	Med	Ave±SD	Range	Med	Ave±SD	Range	Med	Ave±SD	Range	Med	Ave±SD	Range	Med	Ave±SD
Cr	179-850	358	425±192	249-927	368	479±263	1-64	3.4	7±14 A	2-34	5.2	7.6±7.3 A	1.7-20	3.3	4.8±5.5 b	1.9-90	12.4	25±28 a
Co	27-74	42	45±12	22-57	45	40±12	4-13	7	7.3±2.1 B	6-19	12.2	12±3 A	2.1-5	4	3.8±1 b	3.3-15.8	9	8.9±3.6 a
Ni	186-932	408	466±207	247-669	357	410±164	13-164	31	40±35 B	15-140	38.8	50±31 A	12-41	17	21±9 b	25-60	35	40±14 a
Cu	80-467	147	187±111	68-222	103	114±43	15-231	39	63±39 A	28-232	47.9	73±59 A	13-66	19	26±16 b	24-93	47.9	39±21 a
Zn	192-1720	396	510±382	230-559	254	309±113	20-334	66	112±66 A	21-371	65.5	94±90 B	12-135	35	47±38 a	15-106	38.3	48±32 a
As	13-23	18	18±3	7-25	19.9	18±6	0.6-4.1	1.2	1.3±0.8 A	1.3-3.7	2	2.1±0.7 A	0.3-1.5	0.9	0.9±0.4 b	1.3-3.5	2.3	2.4±0.8 a

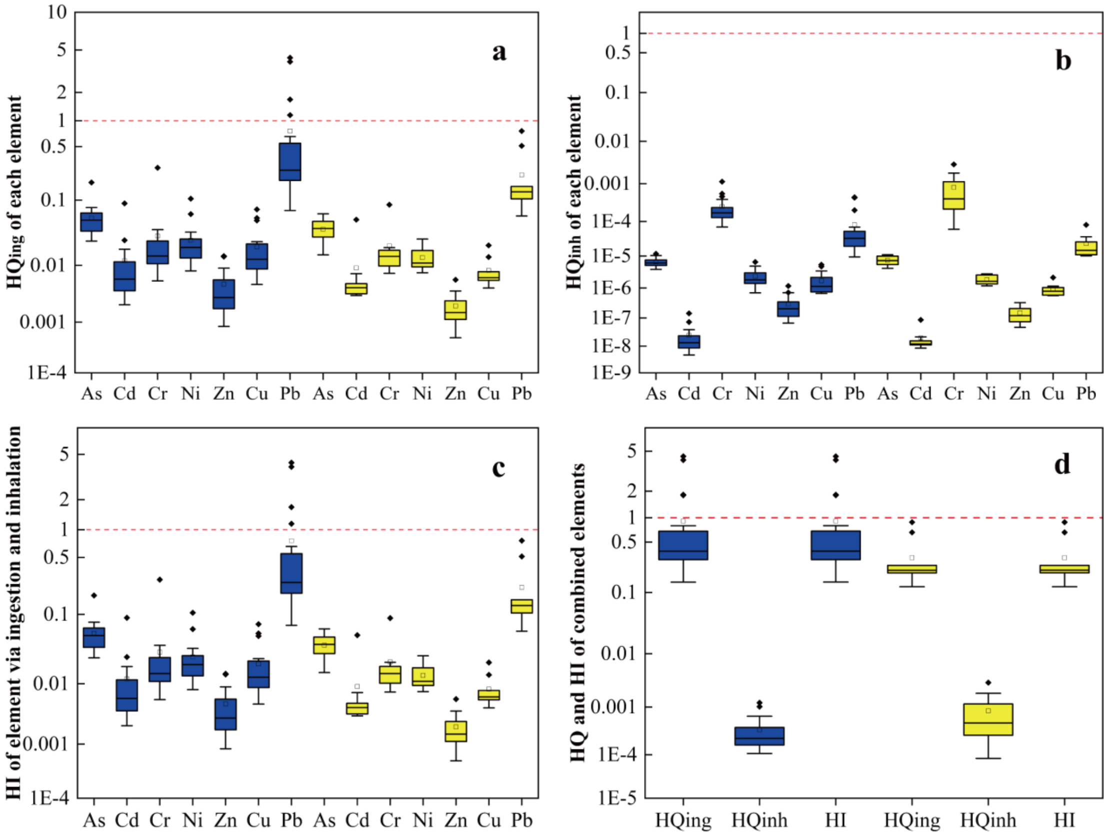
Cd	0.7-11.9	1.3	2.4±2.7	0.8-6.4	1.2	1.7±1.7	0.2-7	0.5	0.9±1.5 A	0.2-6.1	0.6	1.1±1.4 A	0.2-4	0.3	0.7±1.2 a	0.4-3.7	0.51	0.9±1 a
Sb	2-30	5.6	7.9±7.7	1.5-5.8	2.9	3.1±1.3	0.1-1.8	0.3	0.4±0.4 B	0.2-3.9	0.8	1.1±0.9 A	0.1-0.3	0.1	0.1±0.1 b	0.3-1.5	0.6	0.7±0.4 a
Pb	88-3426	286	636±938	90-653	128	200±174	19-1171	69	209±69 B	35-1669	123.7	301±486 A	16-210	36	60±63 b	38-300	55	87±81 a

3.4 Human health risk assessment

The non-carcinogenic and carcinogenic risks due to soil PTE via the ingestion and inhalation exposure pathways are presented in Figures 5 and 6. The mean and median values of HI in this study were lower than 1, suggesting an acceptable average non-carcinogenic risk for the studied soils. However, some sample sites in urban area, children exposure to Pb contaminated soil may have adverse health effects (Fig.5a).

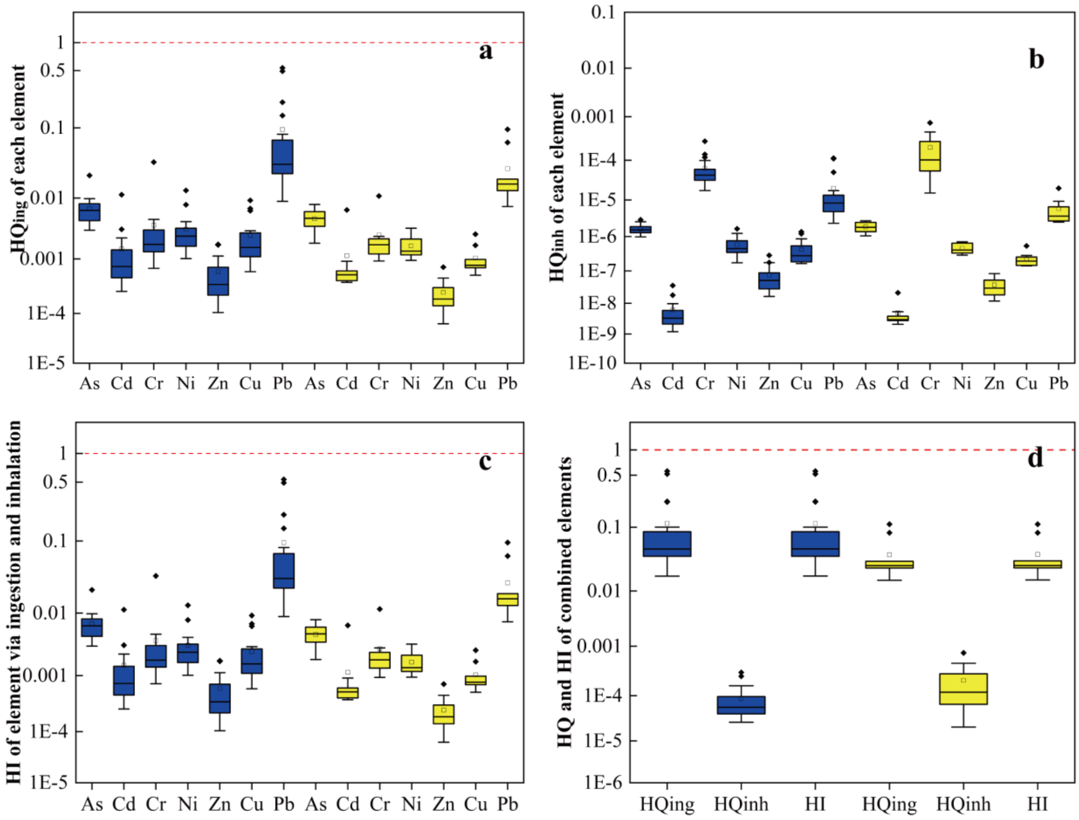
The health risks through the different exposure routes were in the order of ingestion > inhalation (Fig.5 a,b), indicating that exposure to soils due to ingestion contributed to the largest to the total calculated health risk (Zhuo et al., 2019; Liu et al., 2020). Comparatively, non-carcinogenic risks for children were higher than for adults (Fig. 5 1,2), and higher in the urban area than in peri-urban area (Fig.5 d) and the same trend was observed for carcinogenic risk, suggesting that children faced more potential health risks from exposure to elements. The non-carcinogenic risk for each element decreased in the order of Pb > As > Cr > Ni > Cu > Cd > Zn in both areas, which indicated Pb (> 80%) as the main contributor to the estimated human health risk.

In terms of carcinogenic risk, the TCR probabilities for As, Cd, Cr and Pb to children and adults were under the acceptable level ($< 1\times10^{-4}$), indicating no significant risks to adults and children exposed to soils. Soil ingestion was calculated as the most important pathway of exposure (Fig.6 a,b), but inhalation has a higher contribution to the carcinogenic risk than to the non-carcinogenic. Chromium (42%) and As (37%) were the dominant contributor to cumulative carcinogenic risk. This was consistent with previous studies revealing As and Cr being the major carcinogen and Pb the major non-carcinogen factors (Eziz et al., 2018; Fan et al., 2019; Bourliva et al., 2020).


a
HQing of each element
10
5
2
1
0.5
0.1
0.01
0.001
1E-4
As
Cd
Cr
Ni
Zn
Cu
Pb
b
HQinh of each element
0.01
0.001
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
c
HI of element via ingestion and inhalation
d
HQ and HI of combined elements
1E-5
HQing
HQinh
HI

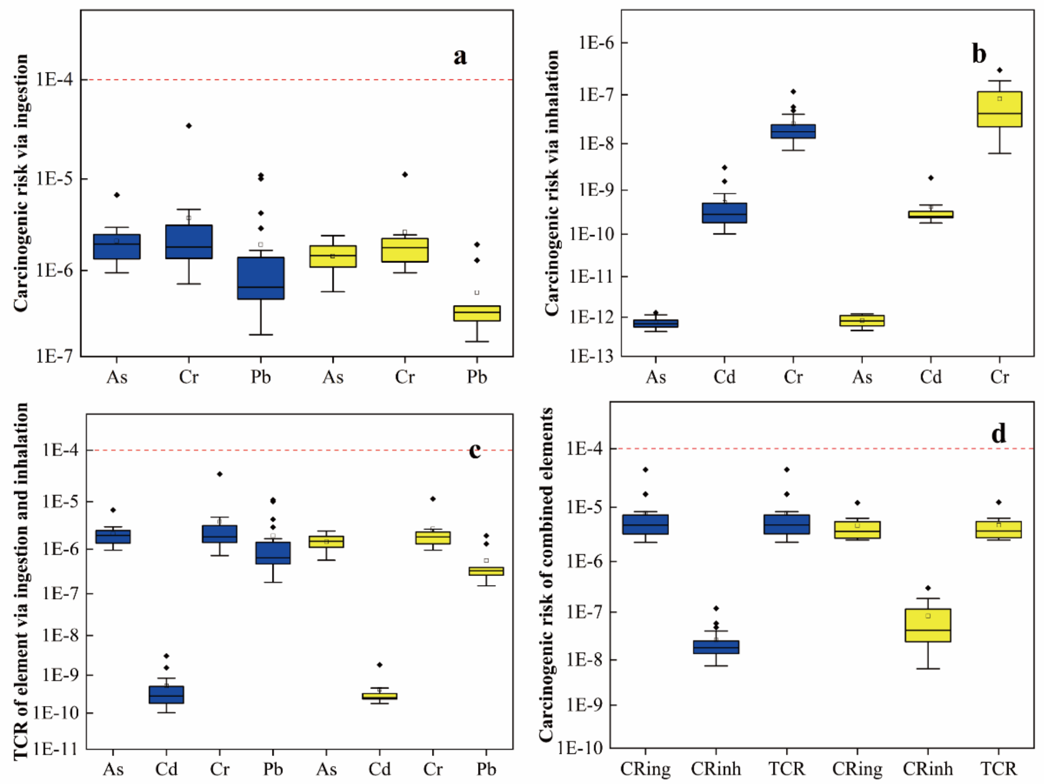
(1)

330

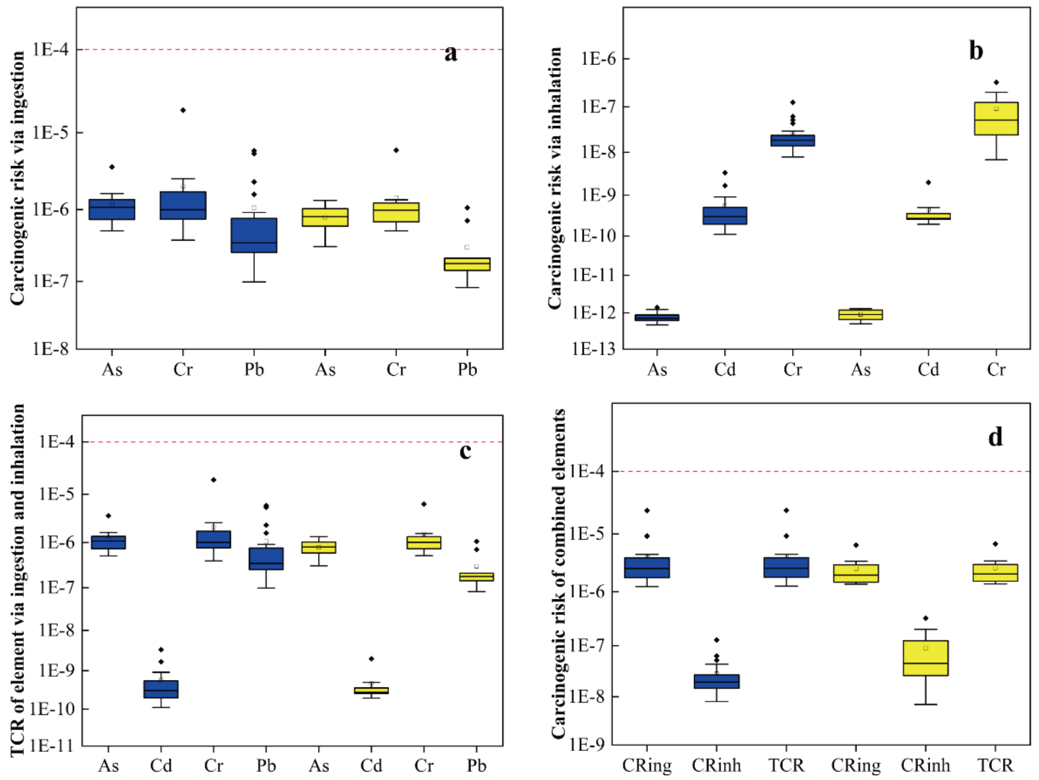


(2)

Figure 5. Non-cancer Hazard Quotients (HQ) and Hazard Indexes (HI) of PTE in urban (blue) and peri-urban (yellow) areas via ingestion and inhalation exposure pathways calculated for children (1) and for adults (2). In detail: (a) HQ of each element through ingestion; (b) HQ of each element through inhalation; (c) HI of each element through ingestion and inhalation; (d) HQ and HI of combined elements through ingestion and inhalation.



(1)



(2)

Figure 6. Cancer risk due to PTE in urban (blue) and peri-urban (yellow) areas via ingestion

and inhalation exposure pathways for children (1) and adults (2). In detail: (a) CR of each element through ingestion; (b) CR of each element through inhalation; (c) TCR of each element through ingestion and inhalation; (d) CR and TCR of combined elements through ingestion and inhalation.

4. Conclusions

In vitro oral and lung bioaccessibility and human health risk assessment of PTE in soil samples from an urban and peri-urban area in Turin were investigated. The average PTE contents and chemico-physical parameters of soils were in line with previous works in the same area. Concerning bioaccessible percentages, they exhibited a decreasing order of Pb > Cd, Cu > Zn > Co > As, Ni, Sb > Cr in the gastric environment and Pb > Cd, Cu > Zn > Co > As, Ni, Sb >Cr regarding lung bioaccessibility. Comparing ingestion and inhalation results, a relative enrichment of bioaccessible concentrations of Pb, Ni, Co and Sb was observed in the inhalable size fraction (< 10 μm) compared to ingestible one. Conversely, the relative bioaccessibility of Pb, Cu, Cd, Zn and As was lower, due to the different components of the extraction solution and extracting pH. The average bioaccessibility values suggested that PTE would more bioavailable if ingested than inhaled. In addition, a higher solubility of Pb, Cd, Zn, and Cu was found using both methods, which may reflect a higher level of anthropogenic pollution.

Human health risk was assessed for the ingestion and inhalation pathways, using the bioaccessible fractions in simulated fluids. Unacceptable non-carcinogenic risk (HQ > 1) was found through ingestion exposure for children in some urban sites and Pb was the most hazardous elements for non-carcinogenic risk. Carcinogenic risks were under the threshold levels for every soil ($CR < 10^{-4}$), with Cr and As being the dominant contributors to risk. Furthermore, children were more susceptible to PTE toxicity than adults and urban area soils posed a higher risk than peri-urban ones. Therefore, this elements, and especially Pb pollution in the urban soils still need more attention, and the necessary soil remediation activities are needed to reduce the risks of human, especially children, exposure to PTE.

Acknowledgements

The first author acknowledges the financial support from the China Scholarship Council (No.201904910524) for his PHD study in University of Turin, Italy.

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