Bioaccessibility of metals and human health risk assessment in community urban gardens

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A B S T R A C T

Pseudo-total (i.e. aqua regia extractable) and gastric-bioaccessible (i.e. glycine + HCl extractable) concentrations of Ca, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined in a total of 48 samples collected from six community urban gardens of different characteristics in the city of Madrid (Spain). Calcium carbonate appears to be the soil property that determines the bioaccessibility of a majority of those elements, and the lack of influence of organic matter, pH and texture can be explained by their low levels in the samples (organic matter) or their narrow range of variation (pH and texture). A conservative risk assessment with bioaccessible concentrations in two scenarios, i.e. adult urban farmers and children playing in urban gardens, revealed acceptable levels of risk, but with large differences between urban gardens depending on their history of land use and their proximity to busy areas in the city center. Only in a worst-case scenario in which children who use urban gardens as recreational areas also eat the produce grown in them would the risk exceed the limits of acceptability.

1. Introduction

In 2000, all United Nations member states signed the Millennium Declaration, which includes the Millennium Development Goals, eight international development purposes to be achieved by the year 2015 addressing, among other aspects, eradication of extreme poverty and hunger and ensuring environmental sustainability (UN, 2001). However, recent world food crises and increasing food prices during the last years prove that we are far away from these targets. A promising strategy in this context is urban agriculture, which has spread worldwide in recent years as it enhances a sustainable urban development and a greener economy. This is even more relevant if we consider the world population projections, which predict an increase of urban population from 3.6 billion in 2011 to 6.3 billion in 2050 (UN, 2012).

Urban agriculture has multiple benefits for human health (physical exercise, well-being, fresh air, sunlight exposure) (Leake et al., 2009; Van den Berg et al., 2010), community betterment (self-supplying food and source of income in developing countries, social network improvement, cultural inheritance preservation) (Ramos and Pinto, 2008) and environmental protection (organic agriculture, agro-biodiversity conservation, organic solid waste recycling by composting, energy saving in transportation and soil erosion reduction) (Brown and Jameton, 2000). However, there are also some drawbacks, and of particular concern is the risk associated with conducting agricultural practices or the ingestion of products grown in potentially contaminated urban soil.

Studies of trace element contents in urban gardens yield alarming results. In Braga (Portugal), all soil samples exceeded the concentration limits for lead and zinc according to Portuguese regulations (Ramos and Pinto, 2008). Cd and Pb contents in urban garden soils located around a smelter in Northern France were 16 and 10 times higher than the respective reference values (Pruvot

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et al., 2006), while in agricultural soils in Castellon, a Spanish Mediterranean region, the levels were higher than the maximum established for horticultural crops in seven of the thirty fields sampled (Peris et al., 2007). Säumel et al. (2012) found that most crop samples from inner city sites had significantly higher trace metal contents than equivalent supermarket samples and that more than half of the samples exceeded standards for Pb concentration in food crops. As a last example, in Wroclaw (Poland), a city with a thermal power station and several chemical and metalworking industries, 35% of urban gardens tested were unsuitable for vegetable production according to Polish quality standards of soil and earth (Kabala et al., 2009).

Most of these soil quality guidelines derive from risk assessments that are based on aqua-regia extractable concentrations in soil and oral toxicity values obtained from studies in which the hazardous substances were administered in a soluble form. Therefore, they may overestimate the risk associated with accidental soil ingestion since only a portion of the elements would be effectively absorbed by the human body (i.e. bioavailable). This fact has generated an increasing interest in incorporating bioavailability into risk assessments (Ge et al., 2002), which is estimated from *in vivo* tests using laboratory animals. However, due to bioethical considerations and to constraints in costs and time, during the last few years *in vitro* extraction tests are being developed to determine the oral bioaccessibility, i.e. the fraction of a substance that is soluble in the gastrointestinal environment and is available for absorption (Ruby et al., 1999), as a conservative estimate of bioavailability: HCl extractions, RBALP (Relative Bioaccessibility Leaching Procedure), SBET (Simple Bioaccessibility Extraction Test) or PBET (Physiologically Based Extraction Test).

The bioaccessibility of trace elements in soil is strongly controlled by soil matrix characteristics. The main soil properties controlling the speciation, mobility and retention of metals are soil pH, redox conditions, organic matter, carbonate and phosphate minerals, clay particles and aluminum, iron and manganese (hydr)oxides (Pelfrêne et al., 2013). Texture, in turn, is an important variable controlling the level of exposure to trace elements in soil: fine particles adhere preferentially to human skin and are more easily resuspended in air, and the accompanying trace elements can thus be inhaled and absorbed through the skin.

Urban gardening is spreading worldwide and so is the concern of following a diet that includes food plants grown in urban sites due to possible exposure to contaminants during farming and recreational activities at these gardens. In consequence, the aims of the present study were: (i) to determine the pseudototal and bioaccessible trace element contents in soils and to explain the differences in the degree of contamination; (ii) to investigate the effect of major elements and soil properties on the bioaccessibility of metals; and (iii) to assess the potential risk for children and adults in those scenarios.

2. Materials and methods

2.1. Study location, soil sampling and preparation

Six urban gardens were selected from those included in the main network of food growers in Madrid (ReHdMad), all of them located in the inner city of Madrid within the M-40 ring road (Fig. 1). Table 1 presents past land uses and the main sources of trace element contamination potentially affecting these gardens. In each urban garden, six sampling points were randomly selected. Composite samples, made up of three subsamples, were collected in each sampling point from the arable soil layer (0–20 cm depth) with a stainless steel hand auger set and transferred into air-tight polyethylene bags for transport to the laboratory. The 36 soil samples were air-dried at room temperature for one week and then oven-dried for 48 h at 105 °C. Dry samples were then gently disaggregated with a rubber mallet, homogenized, passed through a 2 mm plastic-mesh sieving set and divided up in quarters: one for soil characteristics determination, another for trace element content (which was further sieved to <100 μm) and the remaining two were stored as backup samples. Additionally, during the site visit, a field reconnaissance was conducted in order to register aspects that may influence the concentration and bioaccessibility of trace elements in soil, i.e. traffic intensity in the vicinity of the urban garden, use (or not) and type of amendments, type of agricultural practices or produce cultivated. Also a questionnaire was distributed among farmers using the selected urban gardens to estimate the value of exposure factors for the risk assessment (e.g. visiting frequency or age).

2.2. Soil analysis

Soil physicochemical properties were determined on the <2 mm size fraction in order to explore their influence on the bioaccessibility of trace elements: soil pH was measured in a soil/water suspension (1:2.5 w/v), particle size distribution was determined after soil dispersion with a sodium hexametaphosphate solution by the hydrometer method (Bouyoucos, 1936), calcium carbonate content was evaluated using a Bernard calcimeter (Allison and Moodie, 1965) and organic matter by means of a wet oxidation with $K_2Cr_2O_7$ (Walkley, 1935).

Pseudototal contents were determined following an aqua regia extraction protocol (adapted from ISO 11466:1995): 1.5 g of dried soil (<100 μm) were transferred to a polypropylene tube with a mixture of 10.5 mL HCl and 3.5 mL HNO_3, allowing to stand overnight for 16 h. The solution was then heated at 95 °C for 2 h in a mid-temperature graphite digestion block, filtered through Albert paper No. 240 and made up to 50 mL with 1% HNO_3.

Bioaccessible contents were obtained by a simplified bioaccessibility extraction test (SBET) as described by Mingot et al. (2011): 0.5 g of soil (<100 μm), mixed with 50 mL of gastric solution (glycine 0.4 M adjusted to pH 1.5 with HCl), were digested at 37 °C for 1 h in a thermostatized shaker. The mixture was centrifuged at 2000 rpm for 4 min and the supernatant filtered through paper Lab No. 1300/80.

The concentrations of trace and major elements in samples were measured by flame atomic absorption spectrophotometry. Instrument detection limits were 0.03 mg kg^{-1} for Cu, 0.04 mg kg^{-1} for Ni, 0.06 mg kg^{-1} for Co, 0.05 mg kg^{-1} for Ca, Mn and Zn, and 0.17 mg kg^{-1} for Cr, Fe and Pb. A quality assurance and quality control protocol was implemented to assess the accuracy and precision of the extraction and analysis methods: To correct for instrumental drift a multi-element standard test solution was measured every 18 samples (maximum variation was fixed to be ±15%). Six sample triplicates, a blank digestion triplicate and a certified standard reference soil material (WEPAL ISE 987) were included for each batch of 36 samples. The relative standard deviation of the pseudototal replicates was below 10% for all elements, except for Ni (1.81–33.41%). The statistical analyses of the data were carried out using R software (R Development Core Team, 2013).

2.3. Bioaccessibility determination

The average trace element bioaccessibility was estimated in three different ways, depending on the value of the "weight", ω_i, in the general expression:

$$\hat{\beta} = \frac{\sum_{i=1}^{n} x_i y_i \omega_i}{\sum_{i=1}^{n} x_i^2 \omega_i} \tag{1}$$

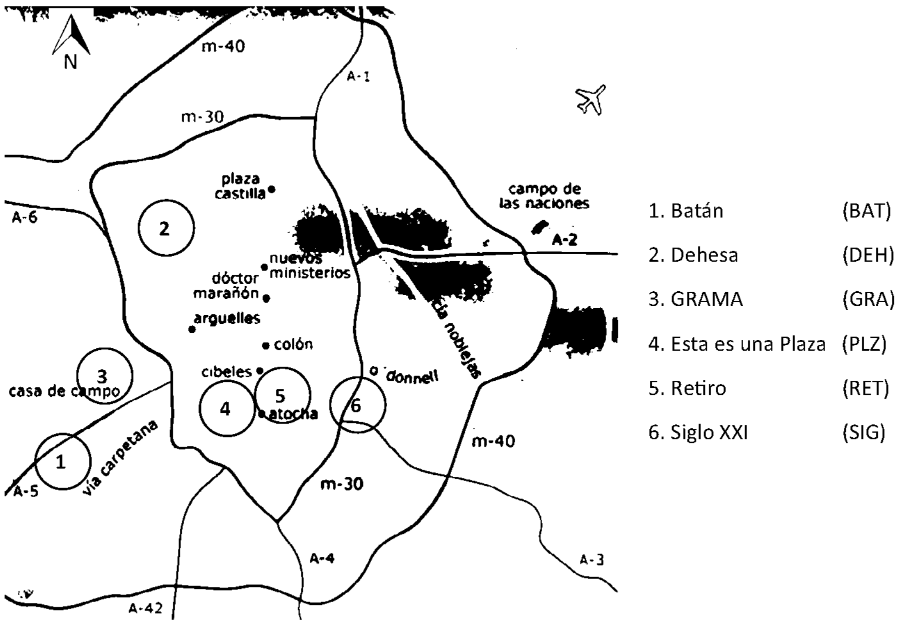

Fig. 1. Location of urban gardens sampled in Madrid.

Table 1
Sources of contamination potentially affecting the urban gardens included in the study.

Urban garden	Description
Batán (BAT)	On a wasteland used as a dump site for brickworks and close to a major road
Dehesa (DEH)	On former plant nurseries and near a bunker from the Spanish Civil War
GRAMA (GRA)	Evidences of parking and waste disposal uses
Esta es una Plaza (PLZ)	Abandoned for over 30 years, previously occupied by a jewelry factory
Retiro (RET)	Next to a plant nursery with fuel-burning heating systems and to the old building of the City Hall workshops (carpentry, locksmith)
Siglo XXI (SIG)	Adjacent to a busy street, with a plant barrier between them

where $\hat{\beta}$ represents the average bioaccessibility (%), and x and y the aqua regia and glycine extractable contents (mg kg^{-1}), respectively. The three equations used were:

$$\hat{\beta} = \frac{\sum_{i=1}^{n} x_i y_i}{\sum_{i=1}^{n} x_i^2} \quad (2)$$

$$\hat{\beta} = \frac{\sum_{i=1}^{n} y_i}{\sum_{i=1}^{n} x_i} \quad (3)$$

$$\hat{\beta} = \frac{1}{n}\sum_{i=1}^{n} \frac{y_i}{x_i} \quad (4)$$

In Eq. (2), ω_i is constant (i.e. all data have the same "weight" since ω_i is independent of x_i) and the average bioaccessibility is calculated as the slope of a linear regression, forced to intercept the origin, of bioaccessible concentrations on pseudototal concentrations, assuming constant variance of residuals and zero bioaccessibility at zero pseudototal concentration. If the weight ω_i is proportional to the inverse of x_i, Eq. (3) is obtained, in which the average bioaccessibility is calculated as the quotient of the sum of bioaccessible concentrations divided by the sum of pseudototal concentrations. Since $\omega_i \propto 1/x_i$, samples with low concentrations exert a stronger influence on the estimate of the average bioaccessibility than samples with high concentrations. Lastly, if $\omega_i \propto 1/x_i^2$, Eq. (4) is obtained, the average bioaccessibility is calculated as the average quotient between each value of bioaccessible concentration divided by the corresponding value of pseudototal concentration, and the estimate is influenced even more strongly (squared) by low values near the origin.

2.4. Exposure assessment and risk characterization

Three possible exposure scenarios were considered: (a) agricultural, where the receptor is assumed to be an adult taking an active role in cultivation and exposed through the routes of direct accidental ingestion of soil, inhalation of resuspended particles, dermal absorption of toxic elements in particles adhered to skin and ingestion of self-produced vegetables; (b) recreational, in which the RME (reasonable maximum exposure) receptors are children playing in the urban gardens and exposed through the same pathways as in the previous case, except for food intake; and (c) recreational + produce ingestion, a worst-case scenario in which children who play in the urban gardens also eat the produce grown in them by their parents. The average daily doses (ADD) and the exposure concentration in air (Cair) were estimated using the standard equations proposed by the US Environmental Protection Agency:

$$\mathrm{ADD}_{\text{soil ingestion}} = \frac{C \times \mathrm{IR}_S \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times 10^{-6} \quad (5)$$

$$C_{\text{air}} = \frac{C \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{PEF} \times \mathrm{AT}} \quad (6)$$

$$\mathrm{ADD}_{\text{dermal contact}} = \frac{C \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times 10^{-6} \quad (7)$$

$$\mathrm{ADD}_{\text{vegetables ingestion}} = \frac{C \times \mathrm{BCF} \times \mathrm{IR}_V \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{AT}} \times 10^{-3} \quad (8)$$

where C (mg kg^{-1}) is the upper limit of the 95% confidence interval of the mean of the aqua-regia concentration calculated with ProUCL 5.0.00 software (USEPA, 2013), multiplied by the average bioaccessibility in Eqs. (5)–(7), and by a bioconcentration (BCF) or soil-to-plant uptake factor (Bechtel, 1998) for the vegetable ingestion exposure pathway (Eq. (8)); EF is the exposure frequency (75 days year^{-1}) estimated from the on-site survey, and for the remaining exposure factors default values were taken from the USEPA (1991, 2004, 2011): exposure duration, ED (30 years for adults and 6 years for children); body weight, BW (70 kg for adults and 15 kg for children); soil ingestion rate, IRS (100 mg day^{-1} for adults and 200 mg day^{-1} for children); particle emission factor, PEF (1.36×10^9 m^3 kg^{-1}); exposed skin area, SA (5700 cm^2 for adults and 2800 cm^2 for children); skin adherence factor, AF (0.07 mg cm^{-2} for adults and 0.2 mg cm^{-2} for children); dermal absorption factor, ABS (0.01 for all elements); bioconcentration factor, BCF (element specific) and vegetable ingestion rate, IRV (3.7 g kg^{-1} day^{-1} for adults and 7.1 g kg^{-1} day^{-1} for children). The averaging time, AT was set at ED $\times$ 365 days for non-cancer and 25,550 days for carcinogenic contaminants.

To characterize the systemic and carcinogenic risk, a Hazard Index (Eq. (9)) and a level of Cancer Risk (Eq. (10)) respectively, were determined using the corresponding reference dose (RfD), reference concentration (RfC), slope factor (SF) or unit risk (UR), and assuming additivity of adverse health effects for mixtures of elements and multiple exposure routes.

$$\mathrm{HI} = \sum_i \mathrm{HQ}_i \quad \mathrm{HQ} = \frac{\mathrm{ADD}[C_{\mathrm{air}}]}{\mathrm{RfD}[\mathrm{RfC}]} \tag{9}$$

$$\mathrm{RISK} = \sum_i \mathrm{RISK}_i \quad \mathrm{RISK}_i = \mathrm{ADD}[C_{\mathrm{air}}] \cdot \mathrm{SF}[\mathrm{UR}] \tag{10}$$

Chemical specific parameters and toxicity values used in the analysis were taken from the U.S. Department of Energy's RAIS database (USDoE, 2013), except for Pb, whose reference doses have been derived from the World Health Organization's Guidelines for Drinking Water Quality (WHO, 1993). Dermal toxicity values have been determined from oral values, multiplying reference doses and dividing slope factors by a gastrointestinal absorption factor (GSI, 2013).

3. Results and discussion

3.1. Soil characteristics

The range of pH values in the urban gardens included in this study was narrow, varying between 6.72 and 7.78. Texture was also quite homogenous (i.e. sandy loam), with clay fraction contents in all urban gardens below 16%. Average carbonate contents ranged between 1.5% and 10%, and the level of organic matter was generally low (<1.5%), with only a limited number of samples collected from soils with organic amendments presenting concentrations between 2% and 5%.

3.2. Elemental contents

Table 2 summarizes the analytical results for the aqua regia extracts in urban garden soil samples of Madrid. Average concentrations are similar to those reported by De Miguel et al. (1998) for Madrid's urban soil, except for Cr, whose concentration is lower in this study. In the case of Pb, the average concentration in urban gardens exceeded the permissible value of 75 mg kg^{-1} for agricultural land use in Madrid. Results from other research groups are presented in Table 3. Although sampling, preparation and analytical methods are relatively different, overall contents are in the same range, except for Pb, which is particularly high in two urban gardens (PLZ and RET) in this study.

Average concentrations varied widely among urban gardens, reaching differences of up to one order of magnitude for certain elements. A multiple contrast (Tukey) test revealed a significant difference (at p-value < 0.05) between the mean concentrations in the different urban gardens of all trace elements except Co and Mn. This high spatial variability occurred not only between gardens, but also within the same garden. Large intra-garden deviations could usually be explained by the occurrence of singular samples with specific characteristics different from those of the rest within the same urban garden (for example, presence of debris, native vs. tilled or amended soil, different substrate treatment, or affected by industrial activities that did not influence other sampling locations).

A cluster analysis using scaled data, Ward's method and Euclidean distance, revealed that the urban gardens included in the study could be divided in two large groups, with the degree of contamination arising from previous land uses as clustering factor (Fig. 2). On the one hand, urban gardens grouped in Cluster 1 exhibited the highest concentrations of typically urban/industrial trace elements: Cu, Pb and Zn. Two of these gardens (PLZ and RET) are located in the city center and their soil has sustained atmospheric deposition and direct waste disposal from onsite industrial activities (foundry and jewelry production, blacksmith workshop). The third urban garden in this first group was formerly an unpaved parking lot. On the other hand, there is no evidence that polluting activities have taken place in or near the three urban gardens grouped in Cluster 2.

3.3. Bioaccessibility

Results of average bioaccessibility obtained with Eqs. (3) and (4) are similar but differ from those arrived at with Eq. (2) (Table 4). These differences are due, as explained in Section 2.3 to the higher influence of low values on the estimates using Eq. (3) and even more pronouncedly with Eq. (4), while the slope of the linear regression in Eq. (2) is weight-balanced and all data exert the same influence. In Table 4, p-values of the slope estimator (considering

Table 2
Pseudototal contents (in mg kg^{-1}) in urban gardens of Madrid (mean value ± standard deviation, minimum–maximum).

Site	Ca	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
BAT	6616 ± 6799	6.88 ± 0.83	11.71 ± 1.63	19.38 ± 6.01	23039 ± 1429	482 ± 51	5.81 ± 0.85	42 ± 23	104 ± 12
	(2276–20,352)	(6.06–7.99)	(9.92–14.69)	(11.68–29.17)	(20,817–24,528)	(418–551)	(4.89–7.17)	(15–69)	(92–119)
DEH	1135 ± 343	5.99 ± 0.35	11.77 ± 1.69	13.56 ± 1.56	23,015 ± 1774	385 ± 70	6.95 ± 0.72	25 ± 3	83 ± 6
	(759–1606)	(5.67–6.46)	(8.60–13.09)	(11.30–15.98)	(21,264–25,725)	(272–455)	(5.97–7.71)	(20–29)	(72–88)
GRA	2677 ± 1575	6.68 ± 0.51	20.23 ± 4.93	40.98 ± 12.87	18,841 ± 1091	434 ± 60	11.86 ± 1.98	63 ± 31	191 ± 74
	(612–5275)	(6.26–7.66)	(15.60–29.45)	(20.92–58.84)	(17,460–19,862)	(359–512)	(9.39–15.03)	(33–119)	(99–309)
PLZ	65,794 ± 45,228	6.15 ± 0.97	12.93 ± 4.45	72.51 ± 58.44	16,252 ± 3142	417 ± 165	13.27 ± 7.59	239 ± 242	147 ± 72
	(16,308–118,230)	(4.89–7.63)	(4.67–17.93)	(16.13–171.60)	(11,667–20,828)	(285–738)	(6.66–27.89)	(36–598)	(76–260)
RET	34,593 ± 43,913	6.35 ± 0.69	29.76 ± 19.00	50.00 ± 18.21	17,305 ± 2978	371 ± 83	8.54 ± 4.67	200 ± 134	202 ± 41
	(5541–121,650)	(5.52–7.24)	(12.47–57.19)	(22.65–65.00)	(11,897–20,356)	(225–453)	(1.51–14.27)	(95–460)	(143–248)
SIG	5982 ± 4596	5.33 ± 0.39	15.16 ± 4.04	23.16 ± 3.55	18,209 ± 785	451 ± 23	7.67 ± 0.75	45 ± 8	107 ± 22
	(1475–14,001)	(4.89–5.79)	(11.95–22.87)	(16.33–26.84)	(17,003–19,272)	(425–488)	(6.77–8.97)	(30–55)	(80–144)

Table 3
Comparison with other urban soils with agricultural use (mean concentrations in mg kg^{-1}).

Study	Co	Cr	Cu	Mn	Ni	Pb	Zn
Madrid urban gardens	6.09	16.93	36.60	423.46	9.02	98.46	139.17
Szolnoki et al. (2013): Urban gardens, Hungary	6.09	31.32	59.01		22.62	15.71	80.17
Kabala et al. (2009): Allotment gardens, Poland			62.6			91.7	252
Mikula and Indeka (1997): Allotment gardens, Poland		8.4	9.1	219		8.8	313
Ruiz-Cortés et al. (2005): Areas of agricultural use in Seville, Spain		35.0	42.4	394	19.5	156	91.6
Luo et al. (2011): Vegetable garden, China		12.3	324		8.83	95.6	122
Pelfrêne et al. (2012): Agricultural soils, France						153	311

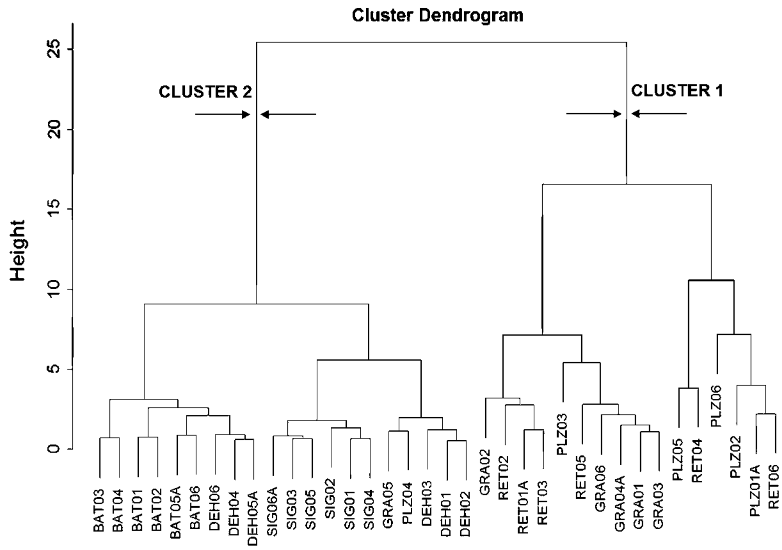

Fig. 2. Cluster analysis of samples (linkage method: ward; distance measure: euclidean).

Table 4
Average gastric bioaccessibility using three different mathematical models.

Equation	Co	Cr	Cu	Mn	Ni	Pb	Zn
$\beta(2)$	32.21	8.15***	39.43***	39.73**	25.37***	46.54***	16.69
$\beta(3)$	37.0*	4.66***	24.62***	40.23***	31.61	59.38***	21.65*
$\beta(4)$	33.46	6.20***	30.50***	40.04**	26.84*	54.27***	19.88

* p-value < 0.05.
** p-value < 0.01.
*** p-value < 0.001.

slope = 0 as the null hypothesis) for the 3 models are also reflected. These estimators were significant for most elements, except for Co and Zn calculated with Eqs. (2) and (4), and Ni using Eq. (3).

There are large differences in the bioaccessibility of the different elements, ranging from less than 10% for Cr up to 90% for Pb in some samples, which indicates that they are bound to different fractions of the soil (carbonate, organic matter, clay surfaces, (hydr)oxides) and with different strengths. Average bioaccessibilities followed the order Pb > Mn > Co > Ni $\approx$ Cu > Zn $\gg$ Cr. The sequence does not exactly coincide with the one determined by De Miguel et al. (2012) in playground soils in Madrid: Cu = Pb = Zn > Co > Ni > Cr, but neither is the soil matrix the same.

To check the influence of soil properties on the bioaccessibility of trace elements simple and multiple linear models were conducted. A relationship could not be established with soil pH or texture, probably because of the low variability of these parameters. Likewise, organic matter content did not affect bioaccessibility, except for Mn with which there is a positive correlation. On the other hand, bioaccessibility was found to depend significantly on the concentration of calcium carbonate for Co, Cu, Ni and Pb. This correlation, which was positive in all cases, can be explained by the fact that at low pH values, such as those of the gastric phase extraction, the carbonate bound elements can be easily mobilized. However, after they enter the intestine, the neutral environment would probably cause the precipitation or the re-adsorption of these elements, reducing the amount that is actually bioavailable (Li and Zhang, 2013; Mingot et al., 2011).

3.4. Risk assessment

The calculated risk for adult urban farmers and for children playing in urban gardens (Table 5) fall below the threshold of unacceptability (HI = 1 or Risk = 10^{-5}), but it has a significant contribution to the overall risk from exposure to trace elements experienced by those receptors in urban environments. The aggregate risk is higher for adults than for children, something expected since in the recreational scenario the food intake pathway was not taken into account. On the other hand, the soil ingestion pathway compared with other exposure routes is proportionally higher for children due to the more frequent hand-to-mouth activity. In the worst-case scenario in which children who play in the selected urban gardens also eat the produce grown in them by their parents,

Table 5
Hazard Quotients and Cancer Risk in the agricultural (adult) and recreational + produce intake (child) scenarios.

Agricultural	Co	Cr	Cu	Mn	Ni	Pb	Zn	$\Sigma HQ/Risk_{Route}$
$HQ_{soil\ ing}$	2.21E−03	1.05E−04	9.14E−05	3.78E−04	4.42E−05	9.24E−03	3.19E−05	1.21E−02
$Risk_{soil\ ing}$		6.76E−08				1.18E−07		1.85E−07
HQ_{dermal}	1.10E−04	1.68E−04	6.40E−06	2.51E−04	4.41E−05	2.46E−03	6.36E−06	3.04E−03
$Risk_{dermal}$		1.08E−07				3.13E−08		1.39E−07
$HQ_{inhalation}$	5.68E−05	1.62E−06		5.44E−04	5.05E−06			6.08E−04
$Risk_{inhalation}$	1.31E−12	5.85E−12			5.07E−14	8.56E−14		7.30E−12
$HQ_{vegetables\ ing}$	5.75E−03	6.01E−03	7.67E−03	8.15E−03	7.89E−03	2.81E−01	1.03E−02	3.27E−01
$Risk_{vegetables\ ing}$		3.87E−06				3.59E−06		7.45E−06
$\Sigma HQ_{Element}$	8.12E−03	6.29E−03	7.77E−03	9.32E−03	7.99E−03	2.93E−01	1.04E−02	HI_T = 0.34
$\Sigma Risk_{Element}$	1.31E−12	4.04E−06	–	–	5.07E−14	3.74E−06	–	R_T = 7.78E−6
Recreat. + prod.	Co	Cr	Cu	Mn	Ni	Pb	Zn	$\Sigma HQ/Risk_{Route}$
$HQ_{soil\ ing}$	2.06E−02	9.82E−04	8.53E−04	3.52E−03	4.12E−04	8.62E−02	2.97E−04	1.13E−01
$Risk_{soil\ ing}$		1.26E−07				2.20E−07		3.46E−07
HQ_{dermal}	7.21E−04	1.10E−03	4.19E−05	1.64E−03	2.89E−04	1.61E−02	4.16E−05	1.99E−02
$Risk_{dermal}$		1.41E−07				4.10E−08		1.82E−07
$HQ_{inhalation}$	5.68E−05	1.62E−06		5.44E−04	5.05E−06			6.08E−04
$Risk_{inhalation}$	2.63E−13	1.17E−12			1.01E−14	1.71E−14		1.46E−12
$HQ_{vegetables\ ing}$	5.15E−02	5.39E−02	6.87E−02	7.29E−02	7.07E−02	2.52E+00	9.25E−02	2.93E+00
$Risk_{vegetables\ ing}$		6.92E−06				6.43E−06		1.34E−05
$\Sigma HQ_{Element}$	7.28E−02	5.59E−02	6.96E−02	7.87E−02	7.14E−02	2.62E+00	9.29E−02	HI_T = 3.06
$\Sigma Risk_{Element}$	2.63E−13	7.19E−06	–	–	1.01E−14	6.69E−06	–	R_T = 1.39E−5

both systemic and carcinogenic risks exceed the standard limits of acceptability and, as in the case of adult farmers, produce intake is by far the exposure pathway with the highest contribution to the overall risk experienced by those receptors.

Among the suite of elements included in the study, the largest contributor for systemic toxicity is lead, which accounts for 85% of the aggregate Hazard Index in the agricultural and worst-case scenarios and 77% in the recreational scenario. For carcinogenic risk, lead and chromium, the only two elements among those analyzed with carcinogenic effects through the route of ingestion, have a similar contribution. These results are consistent with those obtained by Sipter et al. (2008) in their site-specific risk assessment of contaminated vegetable gardens. With respect to the contribution of the different exposure routes, vegetable ingestion accounts for 95% of the total risk in the agricultural and worst-case scenarios and accidental soil ingestion has the highest contribution in the recreational scenario, while dust inhalation is negligible in all cases.

Several uncertainties affecting the results of the risk estimates must be acknowledged. Regarding food intake, the exposure parameters used in the risk assessment may overestimate the risk because bioaccumulation factors are quite conservative, since they are not specific for a particular plant species. Additionally, a bioaccessibility factor from vegetables to humans should also be determined, as has been done with soil. Of particular influence in the quantitative results of the risk assessment is the conservative decision to include lead as a systemic toxic element with an oral Reference Dose derived from the WHO's Guidelines for Drinking Water Quality, despite its apparent lack of threshold. Had lead been included only as a carcinogen, the output of the systemic risk assessment would have been almost an order of magnitude lower and acceptable for the three scenarios considered. Finally, additive effects of contaminants was assumed, but the combined intake of trace elements may result in antagonistic or synergistic effects.

4. Conclusions

As urban gardening increases worldwide, so does the concern that conducting agricultural practices or ingesting products grown in potentially contaminated urban soil might result in adverse health effects. A risk assessment, using gastric-bioaccessible concentrations and several simplifying assumptions that may tend to overestimate risk results in unacceptable levels of risk for a worst-case scenario in which children who use urban gardens as recreational areas also eat the produce grown in them. These quantitative results should be interpreted with caution since they arise from a risk assessment model which incorporates highly conservative assumptions. They do highlight, however, the need for a site-specific assessment of the soil quality in urban gardens since the numerical estimate of risk significantly varies among them, depending on the history of past industrial activities at the site and the rate of deposition of urban aerosol. Pb and Cr are the elements of most concern among those analyzed. For children only playing in urban gardens, the highest level of risk is associated with accidental ingestion of soil particles during games, whereas for adult farmers and children who eat the garden produce the most significant exposure pathway is ingestion of vegetables.

The use of bioaccessible concentrations has a significant impact on the numerical results of the risk assessment: if bioaccessibility had not been taken into account, the results of the risk assessment with a standard pseudototal (i.e. aqua regia) extraction would have indicated an unacceptable level of carcinogenic risk in all the considered scenarios. Bioaccessibilities range from less than 5–8% (depending on the mathematical model used to calculate them) for Cr to 46–60% for Pb. For the soils analyzed in Madrid, with very uniform pH values and clay contents, and with low levels of organic matter, calcium carbonate seems to be the determining factor that explains those differences in bioaccessibility.

Besides bioaccessibility, other sources of uncertainty need to be addressed in future studies in order to guarantee that urban agriculture is not only an environmentally friendly and community-bettering practice but also a safe one. Probably the most important among them is the need to include in the risk assessment toxic metalloids and nonmetals – like arsenic, selenium or antimony – that were not analyzed in this study. Equally important, given that consumption of vegetables grown in urban gardens appears to be the most significant exposure pathway for urban farmers, is to determine reliable vegetable-and-element specific soil-to-plant transfer factors. Lastly, exposure frequency and ingestion rates are critical variables that strongly influence the numerical output of the risk assessment. Although default values taken from the scientific literature provide a valid indication, these variables are population-specific and need to be determined locally.

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