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

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HIGHLIGHTS

- In a worst-case scenario, urban agriculture might pose an unacceptable risk.
- Estimates of bioaccessibility depend significantly on the calculation method used.
- Concentrations of metals vary depending on location and history of land use.
- Calcium carbonate controls the retention of most metals in soil in this study.
- Lead and chromium are the main contributors to risk for human health.

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ABSTRACT

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 $0.03\ \mathrm{mg\,kg^{-1}}$ for Cu, $0.04\ \mathrm{mg\,kg^{-1}}$ for Ni, $0.06\ \mathrm{mg\,kg^{-1}}$ for Co, $0.05\ \mathrm{mg\,kg^{-1}}$ for Ca, Mn and Zn, and $0.17\ \mathrm{mg\,kg^{-1}}$ 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:

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