Urban geochemistry of lead in gardens, playgrounds and schoolyards of Lisbon, Portugal: assessing exposure and risk to human health

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Abstract

To assess the impact of potentially harmful elements in soil/dust on the health of children that use urban recreational areas to play outdoors, an urban survey of Lisbon, the largest city in Portugal was carried out, collecting soils and dusts from public gardens, parks, playgrounds and schoolyards. An exposure and risk assessment study for the incidental soil/dust ingestion of lead was carried out based on US EPA guidelines using a sub-set of 19 topsoil and 8 outdoor dusts, out of a total of 51 samples, incorporating oral bioaccessibility measurements using the Unified BARGE Method developed by the Bioaccessibility Research Group of Europe. The objectives are: (i) interpretation of soil and dust oral bioaccessibility measurements; (ii) assessment of site-specific exposure and non-carcinogenic risk posed by lead; (iii) hazard assessment for urban soil and dust with respect to children playing in outdoor recreational areas. The results show that significant fractions of Pb occur in bioaccessible forms, 24-100% in soils and 35-100% in dusts and the associated risk is greater for dust ingestion than for soil ingestion in Lisbon city recreational areas.

Keywords: urban recreational areas, lead, oral bioaccessibility, health risk assessment, children
Due to their physiological and behavioural characteristics, children are exposed to some environmental contaminants to a greater extent than adults. Toxic chemicals in the environment can cause neurodevelopmental disabilities, and the developing brain can be particularly sensitive to environmental contaminants (US EPA, 2009). For example, elevated blood lead (Pb) levels and prenatal exposures to relatively low levels of Pb (e.g. geometric mean value of 80 mg kg⁻¹ (Johnson and Bretsch 2002)) in soil can result in behavioural disorders and reductions of intellectual function in children (Lanphear et al., 2005; Landrigan et al., 2005).

Over the last decade a number of studies have investigated the exposure of children to urban particulate materials since the exposure of children to potentially harmful elements (PHE) in recreational areas is particularly high (during games at school breaks and in public playgrounds after school), with some researchers concentrating their efforts on the chemical and mineralogical composition of playground soil and dust (Ottesen et al., 2008; Okorie et al., 2011; Costa et al., 2012). The ingestion of soil and dust is an important exposure pathway to environmental chemicals and children, in particular, may ingest soil and dust through deliberate hand-to-mouth movements, or unintentionally by eating food that has dropped on the floor (US EPA, 2011; Bacigalupo and Hale, 2012). For example, soil ingestion is referred to in a number of case studies as a probable source of Pb exposure in children with elevated blood Pb levels in some areas (Johnson and Bretsch, 2002; Laidlaw and Filippelli, 2008; Morrison et al., 2012). High concentrations of Pb in urban soils and dusts have become a potential source of risk to children because Pb has become widely dispersed in the urban environment (Charlesworth et al., 2003; Li and Huang, 2007; Morton-Bermea et al., 2008; Laidlaw and Taylor, 2011).

Understanding soil and dust ingestion patterns is an important part of estimating overall exposures to PHE. As such, investigations of soil and dust ingestion rates among young children have led to numerous studies and recommendations with respect to point-estimate values for soil and dust ingestion (Moya et al., 2004; US EPA, 2009; Okorie et al., 2012). The Child-Specific Exposure Factors Handbook (US EPA,
2009) recommends an ingestion rate among young children (2 to 11 years) of 50 mg day\(^{-1}\) for soil and 60 mg day\(^{-1}\) for dust. Usually, the toxicity of an ingested PHE depends, in part, on the degree to which it is absorbed from the gastrointestinal (GI) tract into the body, i.e. on its oral bioavailability. In this study the term bioavailability refers to the relative bioavailability (US EPA, 2007). Different degrees of absorption result from the fact that a PHE in the solid-phase can exist in a variety of physicochemical forms, and not all forms of a given PHE are solubilised in the GI tract (are bioaccessible) and consequently absorbed to the same extent. Because oral reference doses (RfDs) and cancer slope factors (CSFs) are generally expressed in terms of ingested dose (rather than absorbed dose), accounting for potential differences in absorption between different exposure media can be important to site specific risk assessments (US EPA, 2007). Even a relatively small adjustment in oral bioavailability (i.e. absorption) can have significant impacts on estimated risks. Any estimation of the oral bioavailability of soil-bound PHE assumes that the absorption of such PHE depends on its release in the GI tract (Ruby et al., 1999; Oomen et al., 2002). If the soluble fraction is the maximum concentration of contaminant that can reach systemic circulation then bioaccessibility is a key factor limiting bioavailability and can be used as a conservative measure of bioavailability for risk assessment purposes.

If the bioavailability (i.e. absorption) of a contaminant depends on the physicochemical properties of the solid-phase (soil or dust), the solubility also depends on its solid-phase distribution (partitioning of an element in specific physic-chemical phases of the exposure media) (Wragg et al., 2007; Beauchemin et al., 2011; Patinha et al., 2012; Reis et al., 2012). Reliable site-specific data, if available, may be used instead of non-site specific exposure and toxicity factors (US EPA, 2007) and in this sense bioaccessibility is considered to be a site specific parameter.

This paper assesses the impact of Pb in urban soil/dust on the health of children as part of a larger urban survey of Lisbon, the largest city in Portugal, to assess the impact of potentially harmful elements in urban soil/dust on the health of children who use urban recreational areas to play outdoors. Sampling locations include public gardens, parks and playgrounds and schoolyards, which are considered as urban recreational areas for potential exposure through soil and dust ingestion. Although the dermal absorption
pathway is acknowledged, only ingestion was considered in this study because, at this time, chemical
specific dermal toxicity factors (or dermal absorption values ($ABS_d$) were not available. Frequent users of
the spaces who are considered as sensitive receptors are children under the age of 12. The main objectives
are: (i) interpretation of soil and dust oral bioaccessibility measurements; (ii) assessment of site-specific
exposure and non-carcinogenic risk posed by Pb via the ingestion exposure pathway; (iii) hazard
assessment for urban soil and dust with respect to children playing outdoors in recreational areas.

2.1 The study area
The city of Lisbon is the capital of Portugal, has an area of 284 km$^2$, is divided into 53 districts (Fig. 1)
and has about half a million inhabitants (http://www.cm-lisboa.pt). The smaller districts are located near
the Tagus River and also have a higher population density. Such districts represent the older part of the
city and are characterized by a high housing density, predominance of old buildings, narrow and steep
roads, and a high traffic density. The majority of small public gardens and playgrounds under study are
located in this area (Fig. 1).
The altitude of the city varies between the 3 meters along the Tagus River and 226 meters (above sea
level) at the Monsanto forest park. This park occupies an area of approximately 10 km$^2$ and is one of the
largest urban parks in Europe. The topography of the city consists in a series of hills that are probably
relics of ancient volcanic cones.
The land-use is mostly built environment (90 % of housing, pavements, commercial land, etc) with minor
uses as green-land (9%) and agricultural land (1%, mostly private household backyards, some of which
are used to grow vegetables). The climate in the city is Continental Maritime, with rainy winters and dry,
mild summers. During the last three years, the predominant wind direction has been N-NW (Costa et al.,
2012).
As in most cities over the world (De Miguel et al., 2007; Ottesen et al., 2008), the urban soils of Lisbon are a mixture of original mineral soils, transported soils, organic materials, building materials (bricks, paint, concrete, metal), waste, ash and slag. However, soils from the Monsanto Park, located in the Volcanic Complex of Lisbon, show distinct characteristics. The geochemical and mineralogical compositions of these soils are consistent with the underlying geology (Costa et al., 2012). Therefore, samples collected at sites 9, 11, 12, 13, 14, 15 and 44 are classified as residual and in situ soils (Fig. 1). The origin and time in situ of soils collected outside the Monsanto Park is unknown. In this study, outdoor dusts are considered to be solid particles that accumulate on outdoor ground surfaces in urban areas. The four main sources identified for ground-level dust are deposited airborne...
particles, displaced urban soil particles, pavement debris and anthropogenic materials, which were also reported by other authors (Hu et al., 2011, Okorie et al., 2012). In some samples, the amount of traffic related materials is significant and quite evident through the presence large asphalt particles.

Industrial activity in Lisbon is almost insignificant and the city is mainly characterized by economic activities and public services. Present active sources of contaminants to the urban environment are probably traffic related, the Lisnave shipyard (near site 47) and the Portela international airport (sites 19, 20 and 23), which is located in the youngest part of the city where the main land-use is housing.

2.2 Sampling and sample preparation

Soil and dust samples were collected from locations distributed across the city, depending on the location of urban recreational areas such as public parks, public gardens, playgrounds and schools frequently used by children (Fig. 1). The exception was the international airport of Lisbon, which was chosen as it is located within the city perimeter, and it was assessed as a potentially important source of metals to the surrounding soils and dusts. The sampling sites were selected in as regular pattern as possible across a study area of approximately 84 km². In total, 51 samples were collected for the wider study of PHE in urban areas and 19 soils and 8 dusts selected from these for this study of Pb (see section 2.3). At every location, a composite sample was collected which comprised of 3 samples collected from the upper 5 cm of the soil layer at the apexes of a triangle, at an approximate distance of 1 m from each other and mixed to minimize local heterogeneity. Duplicate samples were collected to estimate the sampling error and the lateral variability.

Dust samples were collected from ground-level, and as close as possible to recreational structures such as swings or football goals. The dust was collected using a small brush and a plastic shovel.

In the laboratory, soil samples were air dried in a fan assisted oven at <40 °C and sieved to provide the <250 µm fraction, which is the fraction of interest for oral bioaccessibility studies (Calabrese et al., 1996).
Dusts were sieved to provide the <150 µm size fraction that adheres more readily to the hands (Sheppard and Evenden, 1994).

2.3 Analyses

Soil pH was determined as pH_{CaCl_2} according to the ISO10390:1994 protocol. Organic matter content (OM) of the soil was determined by loss-on-ignition (LOI), at 430ºC for about 16 h (Schumacher, 2002). Cation exchange capacity (CEC) and the exchangeable cations were measured according to the ISO13536-1995 protocol.

Soil and dust samples were digested using *Aqua Regia* at 95ºC and near-total elemental concentrations were determined by ICP-MS at ACME Analytical Laboratories LTD., Canada (for soils) and by ICP-MS at ACTLABS Analytical Laboratory, Canada (for dusts). Precision of the results was determined through the analysis of laboratory replicates, sample duplicates and certified soil reference materials (Soil S1, Laboratory of Radiometric Analysis, Krakow, Poland; 7002, Analytika Co. Ltd, Czech Republic; NCSZC73004, China National Analysis Centre for iron and steel, China). The results show values for precision (expressed as RSD %) as < 10 %, for all elements. The recoveries obtained for Pb in the certified soil reference materials vary between 81 and 107%, within acceptable ranges.

The semi-quantitative mineralogical analysis of a sub-set of samples (26 soil samples in total) was carried out by X-ray diffraction.

In order to determine exposure to Pb by the ingestion of urban soils and dusts, Pb bioaccessibility was determined by subjecting both soil and dust samples to the Unified BARGE Method (UBM), developed by the Bioaccessibility Research Group of Europe (BARGE). The UBM simulates the leaching of a solid matrix in the human GI tract (Wragg et al., 2011) and is a two stage *in vitro* simulation that represents residence times and physicochemical conditions associated with the gastric tract (G phase) and the gastrointestinal tract (GI phase). The methodology has been validated against a swine model for arsenic (As), cadmium (Cd) and Pb in soils (Denys et al., 2012).
The bioaccessible concentrations of Pb were determined on a selected set of 19 soils and 8 dusts (27 samples in total), from the total collected in full study (51 samples). The selection was based on several conditions: (i) location and spatial distribution as it was important to avoid a biased sampling; (ii) inclusion of samples with both high and low total concentrations; and, (iii) proximity of identified probable metal sources (e.g. old petrol stations).

The bioaccessible extracts were analysed by ICP-MS at the University of Aveiro Laboratory and by ICP-AES at the British Geological Survey (BGS) laboratory. Duplicate samples, blanks, the bioaccessibility guidance material BGS 102 and the standard reference material NIST2711a were extracted with every batch of UBM bioaccessibility extractions for quality control. The blanks always returned results that were below the detection limit. For BGS 102 the Pb recovery was 98% and for NIST2711a 101%. Mean repeatability (expressed as RSD %) was 5.6% for the G phase data and 8.8% for the GI phase data, for soils. For dusts, the mean repeatability was 6.5% for the G phase and 37.7% for the GI phase.

Bioaccessible concentrations of Pb in dusts for the GI-phase were not reproducible, but, in this study the concentrations used are those reported to the G-phase as this phase is considered to provide a more conservative estimate of risk (Farmer et al., 2011).

The bioaccessible fraction (%) of Pb in the solid-phase (soil and outdoor dust) is calculated as follows:

\[ BF_{\text{solid-phase}} = \frac{\text{highest UBM extracted lead concentration}}{\text{pseudo total lead concentration}} \times 100 \]  \[ \text{[1]} \]
In this study, exposure was calculated according to a scenario evaluation approach that uses data on chemical concentration, frequency and duration of exposure as well as information on the behaviors and characteristics of the exposed receptor at a given life stage (US EPA, 2011). The considered scenario is urban recreational areas used by children to play outdoors. Since the sensitive receptors are children under 12 years of age, the exposure and risk assessment study has been carried out for 3 separate age groups: 2< 3 years old, 3< 6 years old and 6< 12 years old, based on the guidelines proposed by the US EPA (2009).

2.4.1 Exposure assessment

For many non-cancer effects the potential exposure to contaminated soil/outdoor dust is expressed in the form of the Average Daily Intake (ADI) according to the following equation:

\[
ADI_{soil/dust} = \frac{C \times IR \times ED \times EF}{Body\ Weight \times Averaging\ Time}\]

Where,

\[ADI = \text{Average Daily Intake (mg kg}^{-1} \text{ day}^{-1})\]

\[C = \text{Lead Concentration (mg kg}^{-1})\]

\[IR = \text{Intake Rate (mg day}^{-1})\]

\[ED = \text{Exposure Duration (years)}\]

\[EF = \text{Exposure frequency (days year}^{-1})\]

\[Averaging\ Time = ED \times 365\ days\]

According to USEPA (1992), \(C\) in Eq. [2] is best expressed as an estimate of the arithmetic mean regardless of the distribution of the data. In this study \(C\) is the total concentration of Pb at each site. This approach is used to address the following considerations: (i) the number of samples under study is small and might not be representative of the entire data population (the selection of sites was not random, it was
dependent on criteria such as the total concentrations of PHE and the geographical location); (ii) the main objective is to assess exposure and risk at each recreational area; and, (iii) it allows identification of differences in bioaccessibility measurements and relationships with the physicochemical properties of the soil. The $ED$ considered is the median age for each age group. For non-carcinogenic effects, the time period used for the averaging time is the actual period of exposure (US EPA, 2009). The $EF$ considered is based on the Recommended Exposure Factors for Children (US EPA, 2009) and corresponds to the mean amount of time playing on grass (day year$^{-1}$), which is the highest value for outdoor activities and was selected as a conservative measure. The $IR$ used is 50 mg day$^{-1}$ of soil and outdoor dust (US EPA, 2009).

Separate $ADI$s were calculated for each age group considered and the potential chronic exposure through childhood was then calculated by summing across each life-stage-specific $ADI$ (US EPA, 2009).

### 2.4.1 Non-carcinogenic risk assessment

The potential non-carcinogenic risk from Pb in soils and dusts is expressed as a Hazard Quotient ($HQ$), as suggested by the US EPA guidelines when a reliable site-specific bioaccessible (bioaccessible fraction of the element of concern in the solid-phase) value is available (US EPA 2007). Therefore, the exposure estimate (i.e., ingested dose) is adjusted when calculating the hazard quotient ($HQ$):

$$HQ = \frac{(ADI \times Bf)}{RfD} \quad [3]$$

Where $ADI$ is the average daily intake (mg kg$^{-1}$ day$^{-1}$), $Bf$ is the bioaccessible fraction of Pb or the % of the total amount of Pb that is accessible in the GI tract and $RfD$ is the oral reference dose. However, the US EPA has not established an $RfD$ for Pb and the FAO/WHO PTWI of 25 µg/kg bw per day, established for infants and children (JECFA, 1993), has been associated with a decrease of at least 3 IQ points in children and an increase in systolic blood pressure of approximately 3 mmHg (0.4 kPa) in adults. It has therefore been concluded that the PTWI can no longer be considered health protective and it has since
been withdrawn. In the last report from the Joint FAO/WHO Expert Committee on Food Additives (JEFCA) the Committee states that the health impact associated to a mean dietary exposure estimate of 0.03 μg/kg bw per day is considered negligible (JEFCA, 2011). Therefore, the RfD used in this study is $0.03 \times 10^{-3}$ mg kg$^{-1}$ day$^{-1}$.

3. Results and discussion

3.1. Near total concentration and oral bioaccessibility of Pb in soils and dusts

The results presented in this section report to the sub-set of 19 soils and 8 dust samples selected from the larger PHE study of Lisbon. In general, the soils have a neutral or near neutral pH (median value of 6.8), organic matter content typical of garden soils (median value of 7.3%) and an average CEC (median value of 21.3 cmol kg$^{-1}$).

Sample 14, has both a high content in OM (40.8%) and high CEC (48.3 cmol kg$^{-1}$), and is clearly an odd sample in the data set under study.

The soils under study are sandy in texture with a grain-size distribution that is not correlated to land use or geology of the study area (Costa et al., 2012). The lack of correlation is an expectable result since only sample 14 that is located inside the natural park of Monsanto can be classified as a natural and in situ soil.

The origin of most urban soils under study is unknown.

Figure 2 shows the box & whisker plot of total and bioaccessible Pb concentrations in the soils. The results show that total concentrations range from 6-441 mg kg$^{-1}$ with a median concentration of 108 mg kg$^{-1}$; bioaccessible concentrations (G-phase) range from 6-260 mg kg$^{-1}$ and a median concentration of 65 mg kg$^{-1}$; there is a significant decrease in bioaccessible Pb from the G phase to the GI phase that has a range of 0.4-77 mg kg$^{-1}$ and a median concentration of 16 mg kg$^{-1}$. Such decrease is referred in a number of studies on Pb bioaccessibility (Rodriguez et al., 1999; Wragg et al., 2011; Zia et al., 2011). The higher pH and increased concentration of a number of enzymes used to simulate intestinal phase of bioaccessibility tests probably lead to the complexation and precipitation of Pb from solution (Grøn and
Figure 3 shows the box & whisker plot of total and bioaccessible Pb concentrations in the dusts. Total Pb concentrations have a median value of 152 mg kg\(^{-1}\), which is higher than that of soils. Bioaccessible concentrations of the element in the gastric phase have a median value of 105 mg kg\(^{-1}\) that is also higher than that of soils. As for soil samples, there is an important decrease in the concentrations of bioaccessible Pb from the G-phase to the GI-phase, which has a median value of 11 mg kg\(^{-1}\).

Maps with the spatial distribution (for the set of 19 soil samples under study) of bioaccessible Pb in the G-phase and the corresponding \(B_f\) for soil samples are presented in figure 4. The \(B_f\) varies between 24 and 100\%, and has a median value of 45\%. This variability for \(B_f\) values is probably due to the physical-chemical properties of the Pb species present in the solid-phase. Soils with higher concentrations of bioaccessible Pb are mainly those in the old city. However, the samples soils with the highest \(B_f\) (samples 5 – playground and 27 – schoolyard) do not correspond to the samples with the highest bioaccessible concentration. Particularly, the bioaccessible concentration in soil 27 is only 70 mg kg\(^{-1}\), which is an
average value (Fig. 2) in the set of samples under study. Yet, the $B_f$ is 100% meaning that all Pb in the soil is available for absorption and this has implications in terms of risk assessment.

Figure 5 shows maps with the spatial distribution (for the set of 8 dust samples under study) of bioaccessible Pb in the G-phase and the corresponding $B_f$ for dust samples. The $B_f$ ranges from 35 to 100% and has a median value of 85%. The median value clearly indicates that in the outdoor dusts Pb is more bioaccessible than in the soils. In general, samples with higher concentrations of bioaccessible Pb are those with a higher $B_f$. Considering the set of dusts under study, sample 15 that corresponds to a dust collected in a playground inside de Monsanto Park has low values for both bioaccessible concentration (15 mg kg$^{-1}$) and $B_f$ (35%). Dusts collected at sites 1 and 18 (playgrounds) have relatively low bioaccessible concentrations (44 mg kg$^{-1}$ and 88 mg kg$^{-1}$, respectively) but a correspondent $B_f$ of 89% and 99%, indicating the presence of mobile Pb. For the other samples, increasing concentrations of bioaccessible Pb correspond to increasing $B_f$s.
Comparing the results of soils and dusts it is evident that, for the relatively small set of samples under study, dusts have larger fractions of Pb in bioaccessible forms than soils. Oral bioaccessibility is controlled by a number of solid phase physical properties, including the particle size. According to several authors, the oral bioaccessibility of PHEs increases with decreasing grain-size (Girouard and Zagury, 2009; Juhasz et al., 2011; Meunier et al., 2011), as bigger surface areas increase dissolution. In this study, the size fraction is finer for dust samples and it is probably the reason for a higher bioaccessibility of Pb.
Fig. 4 Maps with the spatial distribution of bioaccessible concentrations in the G phase and Bf% of Pb for soils; the black line identifies the old city and the dashed line enhances sites with extremely high values for the Bf%.
**Figure 5** Maps with the spatial distribution of bioaccessible concentrations in the G phase and Bf% of Pb for dusts; the black line identifies the old city.

Figure 6 shows XY graphs for total concentrations of Pb versus amount of carbonate minerals in the soil (graph I), bioaccessible Pb in the G-phase versus amount of carbonate minerals in the soil (graph II) and Pb $Bf$ versus amount of carbonate minerals in the soil (graph III). These scatterplots show that there is no relationship between the amount of carbonate minerals and the total (graph I) and bioaccessible (graph II) concentrations of Pb in the soils. However, for soil samples with more than 20% of carbonate minerals
there is a negative correlation between the Pb $Bf$ and the amount of carbonate minerals of the soil. In this sense, the carbonates content of the initial soil seems to be a controlling factor on the bioaccessibility of Pb. It is likely that the dissolution of important amounts of carbonates by the acidic G-fluids can result in an important increase of hydroxy carbonate anions available in solution. Under such conditions, perhaps Pb forms insoluble compounds with the hydroxy carbonate anions. It is also likely that the presence of such an amount of carbonates neutralise the acidic pH of the UBM G-compartment making it less aggressive. However, further studies are necessary to support these hypotheses.
Although direct comparisons with results from other studies are to be carried out with caution due to the disparity in sampling and analytical methodologies, some general comments can be made. Such comparison can be useful to give some insight about the data obtained in the present study. Lung et al. (2007) found lower near total (26.5 – 71.2 mg kg\(^{-1}\)) and bioaccessible (0.21 – 4.08 µg g\(^{-1}\)) concentrations of Pb in playground soils from Uppsala, Sweden; Okorie et al. (2011, 2012) reported higher near total (mean values of 11134 and 992 mg kg\(^{-1}\), respectively) and bioaccessible (median values of 1811 and 33 mg kg\(^{-1}\), respectively) concentrations of Pb and lower \(Bf\) (maximum= 53% and 33%, respectively) for urban soils and dusts from Newcastle upon Tyne, NE England; and, Hu et al. (2011) reported lower near total concentration (mean value of 103 mg kg\(^{-1}\)) and lower \(Bf\) (maximum= 59%) for urban dusts from Nanjing, China. Zia et al. (2011) indicate values for fractional bioaccessibility of Pb in the 5-10% range of total Pb concentration. In a study of topsoil data from Glasgow, London, Northampton and Glasgow in the UK, Appleton et al. (2012) found median Pb bioaccessibilities between 38 and 68%. The bioaccessibility of Pb in urban soils and dusts of Lisbon appears to be slightly higher than that reported in the literature. There is no apparent relation between total metal concentrations and the metal fraction that is available for intestinal absorption and, thus it is concluded that soil metal concentrations do not yield an accurate prediction of the health risk associated to the ingestion of contaminated soil/outdoor dust.

### 3.2 Exposure assessment and health risk assessment

In this study exposure and risk are assessed for each sampled site since one of the aims is to evaluate the hazardousness of soils and dusts from several urban recreational areas to the health of the children. For each group the \(ADI\) (reasonable maximum exposure) was obtained using equation [2]. Potential chronic exposure through childhood is expressed as the sum of the \(ADI\)s for the 3 age groups.
The exposure factors for children recommended by the (US EPA 2009) and sensitive receptor characteristics used to carry out the exposure assessment are listed in table 1.

The potential non-carcinogenic risk for Pb in soils and dusts is calculated according to equation [3]. The $HQ$s calculated, at each site, for each age group and for potential chronic exposure through childhood are presented in table 2 for soil and in table 3 for dust samples.

<table>
<thead>
<tr>
<th>Reference Values</th>
<th>2 - &lt;3</th>
<th>3 - &lt;6</th>
<th>6 - &lt;12</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR (mg soil/outdoor dust day$^{-1}$)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>ED (years)</td>
<td>1</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>EF (days year$^{-1}$)</td>
<td>19</td>
<td>27</td>
<td>33</td>
</tr>
<tr>
<td>AT (days)</td>
<td>365</td>
<td>1095</td>
<td>1825</td>
</tr>
<tr>
<td>Body Weight (kg)</td>
<td>13.8</td>
<td>18.6</td>
<td>31.8</td>
</tr>
</tbody>
</table>

At ingestion rate, ED: exposure duration, EF: exposure frequency, AT: averaging time

Although Pb in soils of some urban sites show a $HQ$ above the safety level, on average the recreational areas under study can be considered safe for children. However, considering a potential chronic exposure through childhood, most sites have an estimated $HQ$ that is above the safety level. From the sub-set of samples under study, sites inside the natural park of Monsanto have the lowest estimated $HQ$ values. The $HQ$ is above the safety level ($HQ < 1$) for sites 33 and 39. Site 33 is a small urban garden in a square that is only 20 m away from a petrol station and site 39 is a playground in a small square surrounded by buildings where the soil was collected at a 20 m distance from a bus stop. At these sites, the source of environmental Pb seems to be traffic related. The age group 3-6 years old is more vulnerable to soil contamination as it has the highest $HQ$s.

For dusts, $HQ$s above 1 occur at site 47, a small garden in the old city that is adjacent to a major road of intense traffic and close to the naval shipyard. At this site, the sources of environmental Pb may be vehicular traffic and steel production. Several studies in urban environments (Farmer et al., 2011; Laidlaw & Taylor, 2011; Yuen et al., 2012) indicate that the wide spread use of unleaded fuels has reduced but not
eliminated the anthropogenic sources of Pb related with motoring activities (e.g. additives in lubricants, wear of vehicle components). Considering a potential chronic exposure through childhood, only sites 1 and 15 (Monsanto Park) have an estimated HQ that is below the threshold. Data from this type of assessment indicates the potential health risks from the direct ingestion of dust borne Pb to children from recreational areas in Lisbon. These results point out differences in risk estimates between exposure from Pb in soil and outdoor dust. For soils and outdoor dusts of Lisbon the risk assessment study indicates that (i) on average (i.e., a global HQ estimated for the area based on the average of the concentrations), the estimated HQs are more elevated for dusts; (ii) for individual assessments such as urban recreational areas used by children, using soil or outdoor dust as exposure media results in different risk assessments (e.g. dust at site 39 does not represent a health risk but soil raises some concern. Due to their different characteristics both materials (soil and outdoor dusts) should probably be routinely included in surveys that aim to assess exposure and health risk associated to the ingestion route.

A risk assessment study would ideally include all potential routes of exposure. However, in this study, ingestion of soils/outdoor dusts is the only route considered since, at this time, chemical specific dermal toxicity factors are not available although the EPA makes oral-to-dermal extrapolations for systemic effects (US EPA, 2004). Other sources such as food and water ingestion were not considered as this is a scenario-evaluation approach specific for children playing in outdoor recreational areas.
Table 2. Hazard Quotient ($HQ$) calculated for each age group and for the sum of the ADIs (represents potential chronic exposure through childhood); some summary statistics ($n=19$ soil samples); data in bold indicates values above the safety level.

<table>
<thead>
<tr>
<th>$HQ$ (age groups in years)</th>
<th>$HQ_{\text{chronic}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - &lt;3</td>
<td>0.32 0.34 0.24 0.90</td>
</tr>
<tr>
<td>5</td>
<td>0.92 0.97 0.69 2.58</td>
</tr>
<tr>
<td>6</td>
<td>0.30 0.31 0.22 0.84</td>
</tr>
<tr>
<td>8</td>
<td>0.29 0.31 0.22 0.83</td>
</tr>
<tr>
<td>11</td>
<td>0.05 0.05 0.04 0.14</td>
</tr>
<tr>
<td>14</td>
<td>0.31 0.33 0.24 0.88</td>
</tr>
<tr>
<td>15</td>
<td>0.04 0.04 0.03 0.11</td>
</tr>
<tr>
<td>16</td>
<td>0.36 0.38 0.27 1.01</td>
</tr>
<tr>
<td>18</td>
<td>0.62 0.66 0.47 1.75</td>
</tr>
<tr>
<td>27</td>
<td>0.46 0.49 0.35 1.29</td>
</tr>
<tr>
<td>30</td>
<td>0.32 0.34 0.24 0.90</td>
</tr>
<tr>
<td>31</td>
<td>0.66 0.70 0.50 1.86</td>
</tr>
<tr>
<td>33</td>
<td>1.12 1.18 0.85 3.15</td>
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<tr>
<td>39</td>
<td>1.64 1.73 1.23 4.59</td>
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<tr>
<td>40</td>
<td>0.95 1.01 0.72 2.68</td>
</tr>
<tr>
<td>42</td>
<td>0.73 0.77 0.55 2.04</td>
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<tr>
<td>43</td>
<td>0.76 0.80 0.57 2.13</td>
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<tr>
<td>44</td>
<td>0.23 0.24 0.17 0.65</td>
</tr>
<tr>
<td>47</td>
<td>1.03 1.09 0.78 2.89</td>
</tr>
<tr>
<td>Median</td>
<td>0.46 0.49 0.35 1.29</td>
</tr>
<tr>
<td>Mean</td>
<td>0.59 0.62 0.44 1.64</td>
</tr>
</tbody>
</table>
Table 3. Hazard Quotient (HQ) calculated for each age group and for the sum of the ADIs (potential chronic exposure through childhood); some summary statistics (n=8 dust samples); data in bold indicates values above the safety level.

<table>
<thead>
<tr>
<th>HQ (age groups in years)</th>
<th>HQ chronic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - &lt;3</td>
<td>6 - &lt;12</td>
</tr>
<tr>
<td>1</td>
<td>0.28</td>
</tr>
<tr>
<td>5</td>
<td>0.59</td>
</tr>
<tr>
<td>15</td>
<td>0.09</td>
</tr>
<tr>
<td>18</td>
<td>0.53</td>
</tr>
<tr>
<td>30</td>
<td>0.99</td>
</tr>
<tr>
<td>33</td>
<td>0.75</td>
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<tr>
<td>39</td>
<td>0.74</td>
</tr>
<tr>
<td>47</td>
<td><strong>1.15</strong></td>
</tr>
<tr>
<td>Median</td>
<td><strong>0.66</strong></td>
</tr>
<tr>
<td>Mean</td>
<td><strong>0.64</strong></td>
</tr>
</tbody>
</table>

4. Conclusions

The first study of Pb bioaccessibility in recreational areas of Lisbon, Portugal, assessing the risk from dust and soil has identified the differences between the total and bioaccessible Pb concentrations and hence the impacts on calculated HQs for the two host materials. Total and bioaccessible concentrations of Pb are higher for outdoor dusts than for soils. Major fractions of Pb are in bioaccessible forms and the values of Bf are higher compared to data reported in recent studies. The Bf of Pb in dusts is generally higher than in soils, probably due to the finer grain size used for the dust samples. A negative correlation between the Bf of Pb and the amount of carbonate minerals was found for soil samples with more than 20% of carbonate minerals. The amount of carbonates in the initial soil appears to be one factor controlling the bioaccessibility of Pb, although others not investigated in this study may also have an
influence. Further studies are necessary to confirm and fully understand this mineralogical control on the bioaccessibility of Pb.

In this study, exposure and health risk were assessed according to a scenario-evaluation approach specific for children playing in outdoor recreational areas. For the soil/outdoor ingestion route, in general the recreational areas of Lisbon can be considered safe for the health of the children. However, some playgrounds show values above the safety level for all the studied age groups. However, it is important to point out that the values of the hazard quotient ($HQ$) were obtained with an $RfD$ for Pb (0.03 µg/kg bw per day) that is much more protective of human health than the value of 25 µg/kg bw per day that was withdraw in 2010.

It is clear that the sites inside the Monsanto Park, the biggest green area of the city, are associated with the lowest $HQ$s and do not represent a health risk for children that are frequent users. All of the results, taken in the context of the local geography and closeness to roads and traffic input suggest that the motor vehicle traffic in the city of Lisbon may be a factor on the quality of the urban soils.

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Available from the National Technical Information Service, Springfield, VA and online at http://www.epa.gov/ncea.


