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

25 1. Introduction

26 Due to their physiological and behavioural characteristics, children are exposed to some environmental
27 contaminants to a greater extent than adults. Toxic chemicals in the environment can cause
28 neurodevelopmental disabilities, and the developing brain can be particularly sensitive to environmental
29 contaminants (US EPA, 2009). For example, elevated blood lead (Pb) levels and prenatal exposures to
30 relatively low levels of Pb (e.g. geometric mean value of 80 mg kg^{-1} (Johnson and Bretsch 2002)) in soil
31 can result in behavioural disorders and reductions of intellectual function in children (Lanphear et al.,
32 2005; Landrigan et al., 2005).
33 Over the last decade a number of studies have investigated the exposure of children to urban particulate
34 materials since the exposure of children to potentially harmful elements (PHE) in recreational areas is
35 particularly high (during games at school breaks and in public playgrounds after school), with some
36 researchers concentrating their efforts on the chemical and mineralogical composition of playground soil
37 and dust (Ottesen et al., 2008; Okorie et al., 2011; Costa et al., 2012). The ingestion of soil and dust is an
38 important exposure pathway to environmental chemicals and children, in particular, may ingest soil and
39 dust through deliberate hand-to-mouth movements, or unintentionally by eating food that has dropped on
40 the floor (US EPA, 2011; Bacigalupo and Hale, 2012). For example, soil ingestion is referred to in a
41 number of case studies as a probable source of Pb exposure in children with elevated blood Pb levels in
42 some areas (Johnson and Bretsch, 2002; Laidlaw and Filippelli, 2008; Morrison et al., 2012). High
43 concentrations of Pb in urban soils and dusts have become a potential source of risk to children because
44 Pb has become widely dispersed in the urban environment (Charlesworth et al., 2003; Li and Huang,
45 2007; Morton-Bermea et al., 2008; Laidlaw and Taylor, 2011).
46 Understanding soil and dust ingestion patterns is an important part of estimating overall exposures to
47 PHE. As such, investigations of soil and dust ingestion rates among young children have led to numerous
48 studies and recommendations with respect to point-estimate values for soil and dust ingestion (Moya et
49 al., 2004; US EPA, 2009; Okorie et al., 2012). The Child-Specific Exposure Factors Handbook (US EPA,

50 2009) recommends an ingestion rate among young children (2 to 11 years) of 50 mg day^{-1} for soil and 60
51 mg day^{-1} for dust. Usually, the toxicity of an ingested PHE depends, in part, on the degree to which it is
52 absorbed from the gastrointestinal (GI) tract into the body, i.e. on its oral bioavailability. In this study the
53 term bioavailability refers to the relative bioavailability (US EPA, 2007). Different degrees of absorption
54 result from the fact that a PHE in the solid-phase can exist in a variety of physicochemical forms, and not
55 all forms of a given PHE are solubilised in the GI tract (are bioaccessible) and consequently absorbed to
56 the same extent. Because oral reference doses (*RfDs*) and cancer slope factors (*CSFs*) are generally
57 expressed in terms of ingested dose (rather than absorbed dose), accounting for potential differences in
58 absorption between different exposure media can be important to site specific risk assessments (US EPA,
59 2007). Even a relatively small adjustment in oral bioavailability (i.e. absorption) can have significant
60 impacts on estimated risks. Any estimation of the oral bioavailability of soil-bound PHE assumes that the
61 absorption of such PHE depends on its release in the GI tract (Ruby et al., 1999; Oomen et al., 2002). If
62 the soluble fraction is the maximum concentration of contaminant that can reach systemic circulation then
63 bioaccessibility is a key factor limiting bioavailability and can be used as a conservative measure of
64 bioavailability for risk assessment purposes.
65 If the bioavailability (i.e. absorption) of a contaminant depends on the physicochemical properties of the
66 solid-phase (soil or dust), the solubility also depends on its solid-phase distribution (partitioning of an
67 element in specific physic-chemical phases of the exposure media) (Wragg et al., 2007; Beauchemin et
68 al., 2011; Patinha et al., 2012; Reis et al., 2012). Reliable site-specific data, if available, may be used
69 instead of non-site specific exposure and toxicity factors (US EPA, 2007) and in this sense
70 bioaccessibility is considered to be a site specific parameter.
71 This paper assesses the impact of Pb in urban soil/dust on the health of children as part of a larger urban
72 survey of Lisbon, the largest city in Portugal, to assess the impact of potentially harmful elements in
73 urban soil/dust on the health of children who use urban recreational areas to play outdoors. Sampling
74 locations include public gardens, parks and playgrounds and schoolyards, which are considered as urban
75 recreational areas for potential exposure through soil and dust ingestion. Although the dermal absorption

76 pathway is acknowledged, only ingestion was considered in this study because, at this time, chemical
77 specific dermal toxicity factors (or dermal absorption values (ABS_d) were not available. Frequent users of
78 the spaces who are considered as sensitive receptors are children under the age of 12. The main objectives
79 are: (i) interpretation of soil and dust oral bioaccessibility measurements; (ii) assessment of site-specific
80 exposure and non-carcinogenic risk posed by Pb via the ingestion exposure pathway; (iii) hazard
81 assessment for urban soil and dust with respect to children playing outdoors in recreational areas.

82

83 2.1 The study area

84 The city of Lisbon is the capital of Portugal, has an area of 284 km^2, is divided into 53 districts (Fig. 1)
85 and has about half a million inhabitants (http://www.cm-lisboa.pt). The smaller districts are located near
86 the Tagus River and also have a higher population density. Such districts represent the older part of the
87 city and are characterized by a high housing density, predominance of old buildings, narrow and steep
88 roads, and a high traffic density. The majority of small public gardens and playgrounds under study are
89 located in this area (Fig. 1).
90 The altitude of the city varies between the 3 meters along the Tagus River and 226 meters (above sea
91 level) at the Monsanto forest park. This park occupies an area of approximately 10 km^2 and is one of the
92 largest urban parks in Europe. The topography of the city consists in a series of hills that are probably
93 relics of ancient volcanic cones.
94 The land-use is mostly built environment (90 % of housing, pavements, commercial land, etc) with minor
95 uses as green-land (9%) and agricultural land (1%, mostly private household backyards, some of which
96 are used to grow vegetables). The climate in the city is Continental Maritime, with rainy winters and dry,
97 mild summers. During the last three years, the predominant wind direction has been N-NW (Costa et al.,
98 2012).
99

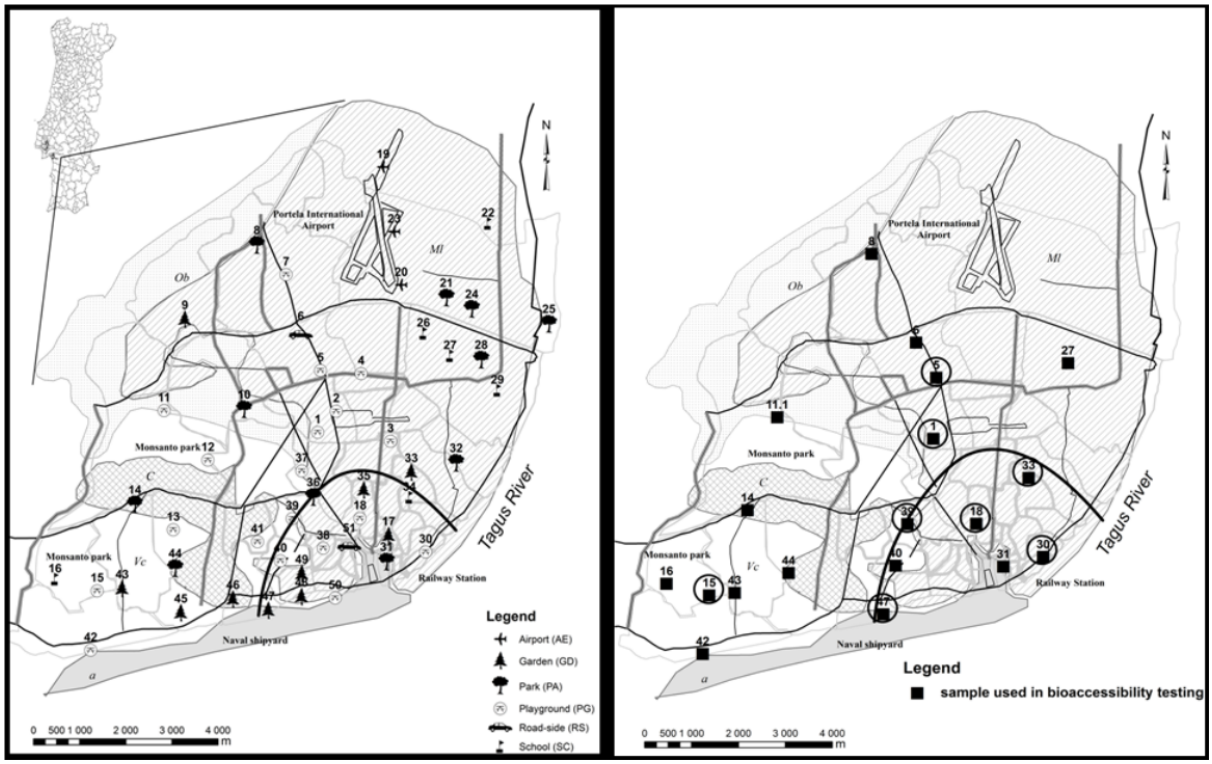

Fig.1 Map A: approximate location of Lisbon city; map of Lisbon showing the location of the 51 sampling sites and the type of recreational area at each site; grey lines outline the 53 districts of the city and larger lines represent higher population density; the black line identifies the old city. Map B: location of 21 soil samples (black squares) and 8 dust samples (black circumferences) used in bioaccessibility testing

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

115 particles, displaced urban soil particles, pavement debris and anthropogenic materials, which were also
116 reported by other authors (Hu et al., 2011, Okorie et al., 2012). In some samples, the amount of traffic
117 related materials is significant and quite evident through the presence large asphalt particles.
118 Industrial activity in Lisbon is almost insignificant and the city is mainly characterized by economic
119 activities and public services. Present active sources of contaminants to the urban environment are
120 probably traffic related, the Lisnave shipyard (near site 47) and the Portela international airport (sites 19,
121 20 and 23), which is located in the youngest part of the city where the main land-use is housing.

122

123 2.2 Sampling and sample preparation
124 Soil and dust samples were collected from locations distributed across the city, depending on the location
125 of urban recreational areas such as public parks, public gardens, playgrounds and schools frequently used
126 by children (Fig. 1). The exception was the international airport of Lisbon, which was chosen as it is
127 located within the city perimeter, and it was assessed as a potentially important source of metals to the
128 surrounding soils and dusts. The sampling sites were selected in as regular pattern as possible across a
129 study area of approximately 84 km^2. In total, 51 samples were collected for the wider study of PHE in
130 urban areas and 19 soils and 8 dusts selected from these for this study of Pb (see section 2.3).
131 At every location, a composite sample was collected which comprised of 3 samples collected from the
132 upper 5 cm of the soil layer at the apexes of a triangle, at an approximate distance of 1 m from each other
133 and mixed to minimize local heterogeneity. Duplicate samples were collected to estimate the sampling
134 error and the lateral variability.
135 Dust samples were collected from ground-level, and as close as possible to recreational structures such as
136 swings or football goals. The dust was collected using a small brush and a plastic shovel.
137 In the laboratory, soil samples were air dried in a fan assisted oven at <40 °C and sieved to provide the
138 <250 μm fraction, which is the fraction of interest for oral bioaccessibility studies (Calabrese et al., 1996).

139 Dusts were sieved to provide the <150 μm size fraction that adheres more readily to the hands
140 (Sheppard and Evenden, 1994).
141
142 2.3 Analyses
143 Soil pH was determined as $pH_{(CaCl2)}$ according to the ISO10390:1994 protocol. Organic matter content
144 (OM) of the soil was determined by loss-on-ignition (LOI), at 430ºC for about 16 h (Schumacher, 2002).
145 Cation exchange capacity (CEC) and the exchangeable cations were measured according to the
146 ISO13536-1995 protocol.
147 Soil and dust samples were digested using *Aqua Regia* at 95ºC and near-total elemental concentrations
148 were determined by ICP-MS at ACME Analytical Laboratories LTD., Canada (for soils) and by ICP-MS
149 at ACTLABS Analytical Laboratory, Canada (for dusts). Precision of the results was determined through
150 the analysis of laboratory replicates, sample duplicates and certified soil reference materials (Soil S1,
151 Laboratory of Radiometric Analysis, Krakow, Poland; 7002, Analytika Co. Ltd, Czech Republic;
152 NCSZC73004, China National Analysis Centre for iron and steel, China). The results show values for
153 precision (expressed as RSD %) as < 10 %, for all elements. The recoveries obtained for Pb in the
154 certified soil reference materials vary between 81 and 107%, within acceptable ranges.
155 The semi-quantitative mineralogical analysis of a sub-set of samples (26 soil samples in total) was carried
156 out by X-ray diffraction.
157 In order to determine exposure to Pb by the ingestion of urban soils and dusts, Pb bioaccessibility was
158 determined by subjecting both soil and dust samples to the Unified BARGE Method (UBM), developed
159 by the Bioaccessibility Research Group of Europe (BARGE). The UBM simulates the leaching of a solid
160 matrix in the human GI tract (Wragg et al., 2011) and is a two stage *in vitro* simulation that represents
161 residence times and physicochemical conditions associated with the gastric tract (G phase) and the gastro-
162 intestinal tract (GI phase). The methodology has been validated against a swine model for arsenic (As),
163 cadmium (Cd) and Pb in soils (Denys et al., 2012).

164 The bioaccessible concentrations of Pb were determined on a selected set of 19 soils and 8 dusts (27
165 samples in total), from the total collected in full study (51 samples). The selection was based on several
166 conditions: (i) location and spatial distribution as it was important to avoid a biased sampling; (ii)
167 inclusion of samples with both high and low total concentrations; and, (iii) proximity of identified
168 probable metal sources (e.g. old petrol stations).
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173 probable metal sources (e.g. old petrol stations).
174 The bioaccessible extracts were analysed by ICP-MS at the University of Aveiro Laboratory and by ICP-
175 AES at the British Geological Survey (BGS) laboratory. Duplicate samples, blanks, the bioaccessibility
176 guidance material BGS 102 and the standard reference material NIST2711a were extracted with every
177 batch of UBM bioaccessibility extractions for quality control. The blanks always returned results that
178 were below the detection limit. For BGS 102 the Pb recovery was 98% and for NIST2711a 101%. Mean
179 repeatability (expressed as RSD %) was 5.6% for the G phase data and 8.8% for the GI phase data, for
180 soils. For dusts, the mean repeatability was 6.5% for the G phase and 37.7% for the GI phase.
181 Bioaccessible concentrations of Pb in dusts for the GI-phase were not reproducible, but, in this study the
182 concentrations used are those reported to the G-phase as this phase is considered to provide a more
183 conservative estimate of risk (Farmer et al., 2011).
184 The bioaccessible fraction (%) of Pb in the solid-phase (soil and outdoor dust) is calculated as follows:

185 $$Bf\%_{solid-phase} = \frac{highest\ UBM\ extracted\ lead\ concentration}{pseudo\ total\ lead\ concentration} \times 100 \qquad [1]$$

186

187 2.4 Exposure and risk assessment

188 In this study, exposure was calculated according to a scenario evaluation approach that uses data on
189 chemical concentration, frequency and duration of exposure as well as information on the behaviors and
190 characteristics of the exposed receptor at a given life stage (US EPA, 2011). The considered scenario is
191 urban recreational areas used by children to play outdoors. Since the sensitive receptors are children under
192 12 years of age, the exposure and risk assessment study has been carried out for 3 separate age groups: 2<
193 3 years old, 3< 6 years old and 6< 12 years old, based on the guidelines proposed by the US EPA (2009).

194

195 2.4.1 Exposure assessment

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

198
$$ADI_{soil/dust} = \frac{C \times IR \times ED \times EF}{Body\ Weight \times Averaging\ Time} \quad [2]$$

199 Where,

200 *ADI* = Average Daily Intake (mg kg^{-1} day^{-1})

201 *C* = Lead Concentration (mg kg^{-1})

202 *IR* = Intake Rate (mg day^{-1})

203 *ED* = Exposure Duration (years)

204 *EF* = Exposure frequency (days $year^{-1}$)

205 *Averaging Time*= *ED*×365 days

206 According to USEPA (1992), *C* in Eq. [2] is best expressed as an estimate of the arithmetic mean
207 regardless of the distribution of the data. In this study *C* is the total concentration of Pb at each site. This
208 approach is used to address the following considerations: (i) the number of samples under study is small
209 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 0.03×10^{-3} mg kg^{-1} day^{-1}.

3. Results and discussion

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

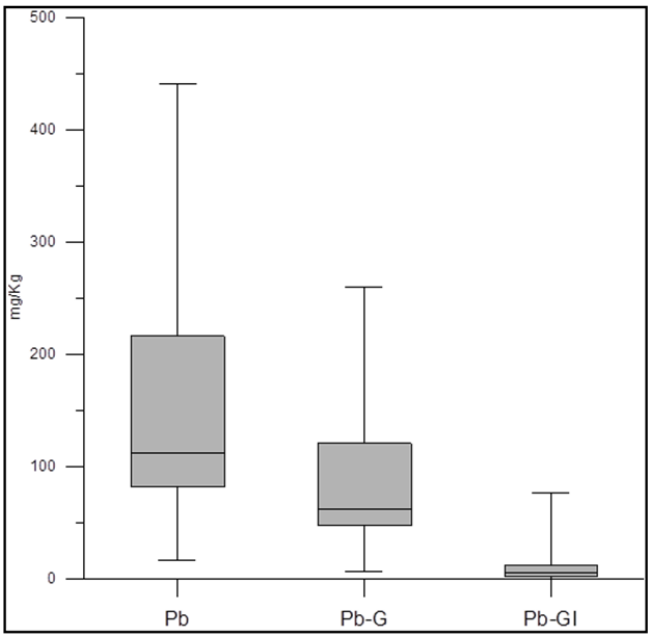
The results presented in this section report to the sub-set of 19 soils and 8 dust samples selected from the larger PHE study of Lisbon.

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

258 Andersen, 2003), resulting in lower bioaccessibility values and poorer reproducibility of results (Wragg et
259 al. 2011).
260 Figure 3 shows the box & whisker plot of total and bioaccessible Pb concentrations in the dusts. Total Pb
261 concentrations have a median value of 152 mg kg^{-1}, which is higher than that of soils. Bioaccessible
262 concentrations of the element in the gastric phase have a median value of 105 mg kg^{-1} that is also higher
263 than that of soils. As for soil samples, there is an important decrease in the concentrations of bioaccessible
264 Pb from the G-phase to the GI-phase, which has a median value of 11 mg kg^{-1}.



265

266 **Fig.2** Box & whisker plot of total and bioaccessible Pb concentrations in soils
267 Maps with the spatial distribution (for the set of 19 soil samples under study) of bioaccessible Pb in the
268 G-phase and the corresponding *Bf* for soil samples are presented in figure 4. The *Bf* varies between 24 and
269 100%, and has a median value of 45%. This variability for *Bf* values is probably due to the physic-
270 chemical properties of the Pb species present in the solid-phase. Soils with higher concentrations of
271 bioaccessible Pb are mainly those in the old city. However, the samples soils with the highest *Bf* (samples
272 5 – playground and 27 – schoolyard) do not correspond to the samples with the highest bioaccessible
273 concentration. Particularly, the bioaccessible concentration in soil 27 is only 70 mg kg^{-1}, which is an

274 average value (Fig. 2) in the set of samples under study. Yet, the *Bf* is 100% meaning that all Pb in the
275 soil is available for absorption and this has implications in terms of risk assessment.
276 Figure 5 shows maps with the spatial distribution (for the set of 8 dust samples under study) of
277 bioaccessible Pb in the G-phase and the corresponding *Bf* for dust samples. The *Bf* ranges from 35 to
278 100% and has a median value of 85%. The median value clearly indicates that in the outdoor dusts Pb is
279 more bioaccessible than in the soils. In general, samples with higher concentrations of bioaccessible Pb
280 are those with a higher Bf. Considering the set of dusts under study, sample 15 that corresponds to a dust
281 collected in a playground inside de Monsanto Park has low values for both bioaccessible concentration
282 (15 mg kg^{-1}) and *Bf* (35%). Dusts collected at sites 1 and 18 (playgrounds) have relatively low
283 bioaccessible concentrations (44 mg kg^{-1} and 88 mg kg^{-1}, respectively) but a correspondent *Bf* of 89% and
284 99%, indicating the presence of mobile Pb. For the other samples, increasing concentrations of
285 bioaccessible Pb correspond to increasing *Bfs*.
286

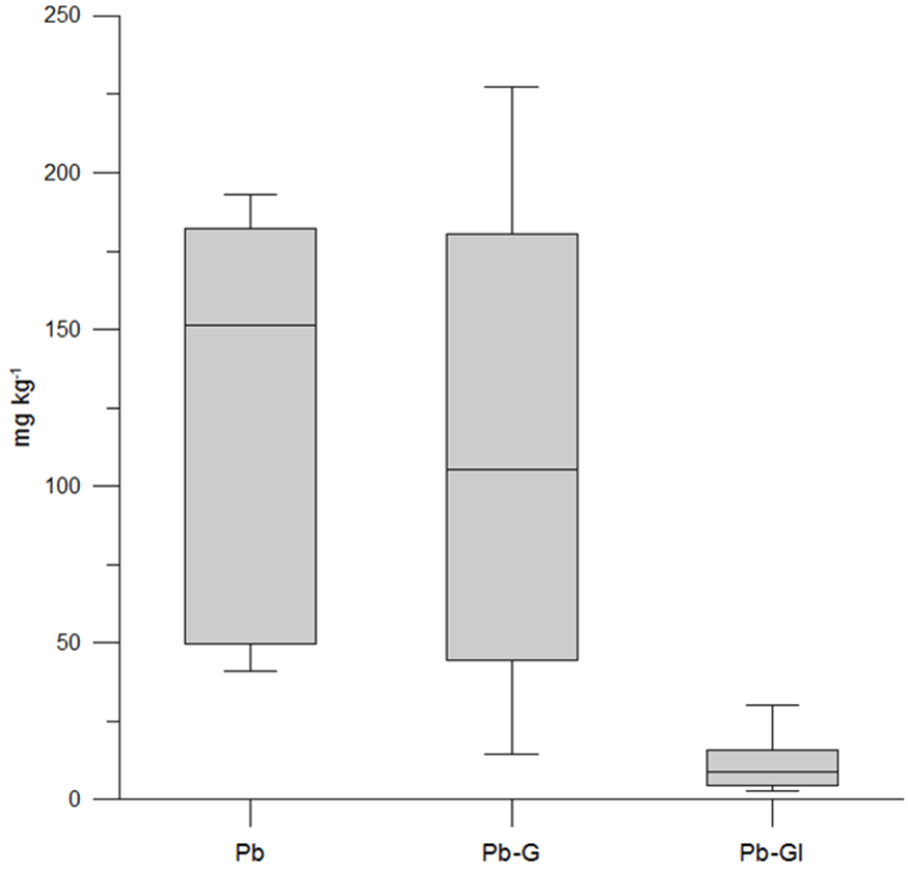
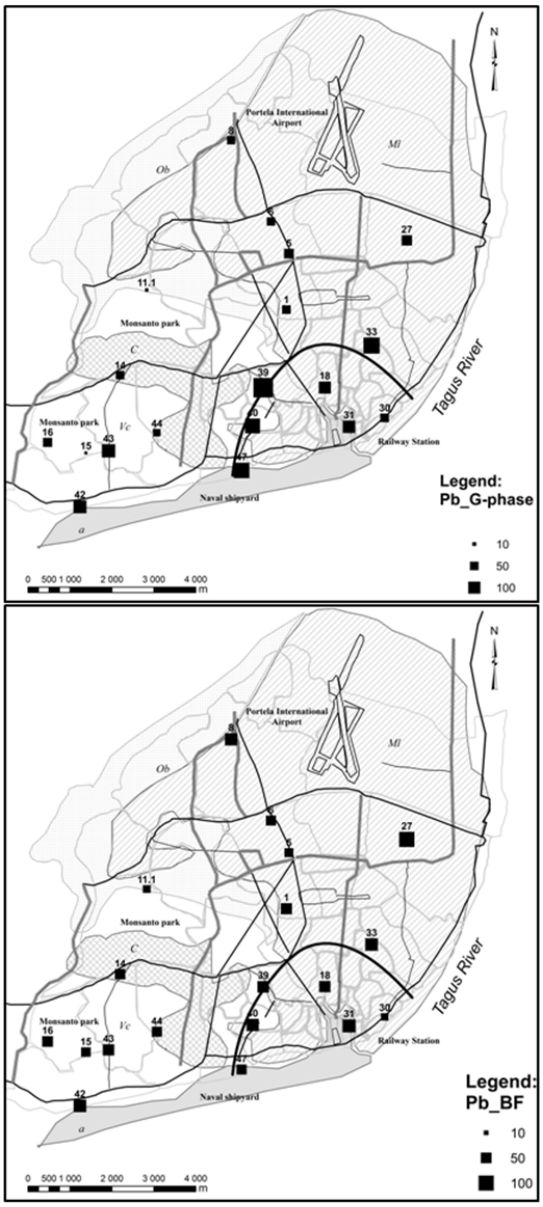


Fig.3 Box & whisker plot of total and bioaccessible Pb concentrations in dusts

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.



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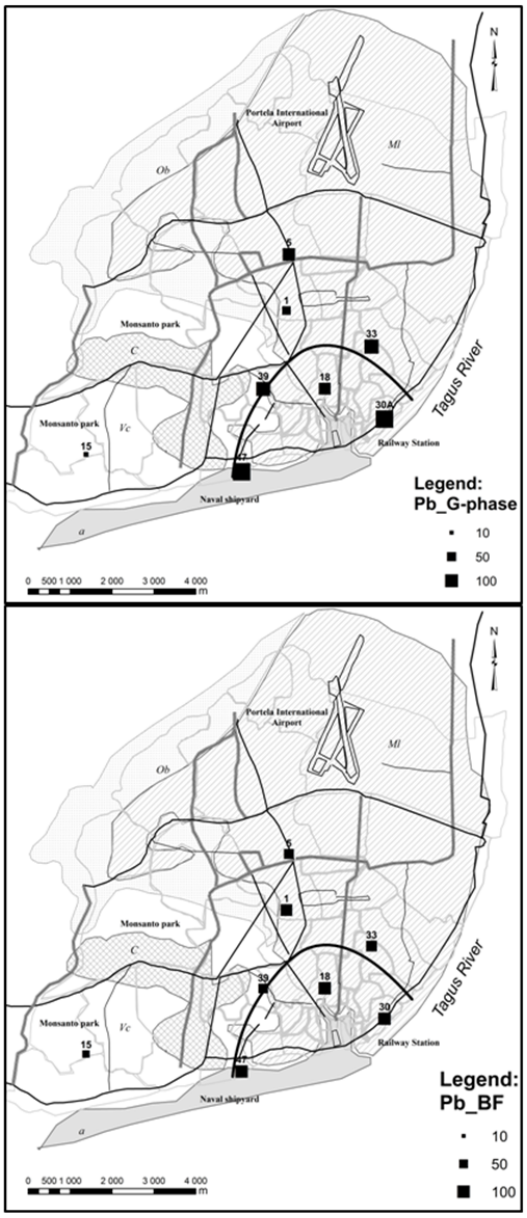
297 **Fig.4** Maps with the spatial distribution of bioaccessible concentrations in the G phase and Bf% of Pb for
298 soils; the black line identifies the old city and the dashed line enhances sites with extremely high values
299 for the Bf%

300

301

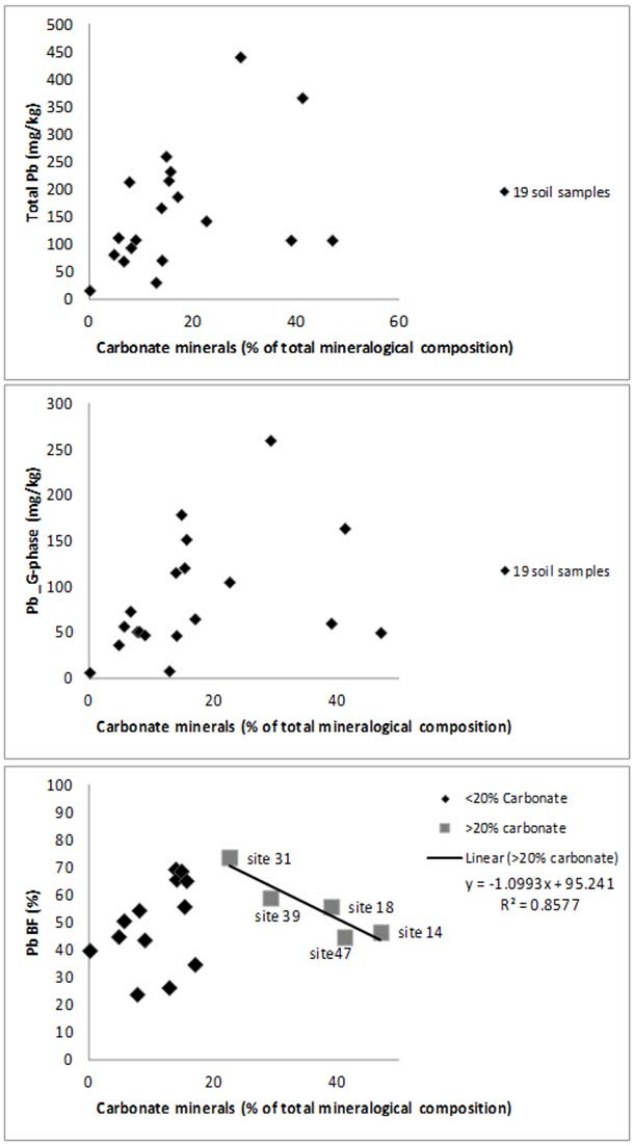


302

303 **Fig.5** Maps with the spatial distribution of bioaccessible concentrations in the G phase and Bf% of Pb for
304 dusts; the black line identifies the old city

305 Figure 6 shows XY graphs for total concentrations of Pb versus amount of carbonate minerals in the soil
306 (graph I), bioaccessible Pb in the G-phase versus amount of carbonate minerals in the soil (graph II) and
307 Pb *Bf* versus amount of carbonate minerals in the soil (graph III).These scatterplots show that there is no
308 relationship between the amount of carbonate minerals and the total (graph I) and bioaccessible (graph II)
309 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.



318 **Fig.6** XY graphs for total concentrations versus % carbonate minerals (graph I), bioaccessible
319 concentrations in the G-phase versus % carbonate minerals (graph II) and Bf versus %carbonate minerals
320 (graph III)

321 Although direct comparisons with results from other studies are to be carried out with caution due to the
322 disparity in sampling and analytical methodologies, some general comments can be made. Such
323 comparison can be useful to give some insight about the data obtained in the present study. Lung et al.
324 (2007) found lower near total (26.5 – 71.2 mg kg^{-1}) and bioaccessible (0.21 – 4.08 µg g^{-1}) concentrations
325 of Pb in playground soils from Uppsala, Sweden; Okorie et al. (2011, 2012) reported higher near total
326 (mean values of 11134 and 992 mg kg^{-1}, respectively) and bioaccessible (median values of 1811 and 33
327 mg kg^{-1}, respectively) concentrations of Pb and lower *Bf* (maximum= 53% and 33%, respectively) for
328 urban soils and dusts from Newcastle upon Tyne, NE England; and, Hu et al. (2011) reported lower near
329 total concentration (mean value of 103 mg kg^{-1}) and lower *Bf* (maximum= 59%) for urban dusts from
330 Nanjing, China. Zia et al. (2011) indicate values for fractional bioaccessibility of Pb in the 5-10% range
331 of total Pb concentration. In a study of topsoil data from Glasgow, London, Northampton and Glasgow in
332 the UK, Appleton et al. (2012) found median Pb bioaccessibilities between 38 and 68%. The
333 bioaccessibility of Pb in urban soils and dusts of Lisbon appears to be slightly higher than that reported in
334 the literature. There is no apparent relation between total metal concentrations and the metal fraction that
335 is available for intestinal absorption and, thus it is concluded that soil metal concentrations do not yield an
336 accurate prediction of the health risk associated to the ingestion of contaminated soil/outdoor dust.
337

338 3.2 Exposure assessment and health risk assessment

339 In this study exposure and risk are assessed for each sampled site since one of the aims is to evaluate the
340 hazardousness of soils and dusts from several urban recreational areas to the health of the children.
341 For each group the *ADI* (reasonable maximum exposure) was obtained using equation *[2]*. Potential
342 chronic exposure through childhood is expressed as the sum of the *ADI*s for the 3 age groups.

343 The exposure factors for children recommended by the (US EPA 2009) and sensitive receptor
344 characteristics used to carry out the exposure assessment are listed in table 1.
345 The potential non-carcinogenic risk for Pb in soils and dusts is calculated according to equation [3].
346 The *HQ*s calculated, at each site, for each age group and for potential chronic exposure through childhood
347 are presented in table 2 for soil and in table 3 for dust samples.
348 Table 1. Recommended exposure factors for children (US EPA 2009).

Reference Values	2 - <3	3 - <6	6 - <12
IR (mg soil/outdoor dust day^{-1})	50	50	50
ED (years)	1	3	5
EF (days year^{-1})	19	27	33
AT (days)	365	1095	1825
Body Weight (kg)	13.8	18.6	31.8

349 IR: ingestion rate; ED: exposure duration; EF: exposure frequency; AT: averaging time

350 Although Pb in soils of some urban sites show a *HQ* above the safety level, on average the recreational
351 areas under study can be considered safe for children. However, considering a potential chronic exposure
352 through childhood, most sites have an estimated *HQ* that is above the safety level. From the sub-set of
353 samples under study, sites inside the natural park of Monsanto have the lowest estimated *HQ* values. The
354 *HQ* is above the safety level (*HQ*< 1) for sites 33 and 39. Site 33 is a small urban garden in a square that
355 is only 20 m away from a petrol station and site 39 is a playground in a small square surrounded by
356 buildings where the soil was collected at a 20 m distance from a bus stop. At these sites, the source of
357 environmental Pb seems to be traffic related. The age group 3-6 years old is more vulnerable to soil
358 contamination as it has the highest *HQs*.
359 For dusts, *HQs* above 1 occur at site 47, a small garden in the old city that is adjacent to a major road of
360 intense traffic and close to the naval shipyard. At this site, the sources of environmental Pb may be
361 vehicular traffic and steel production. Several studies in urban environments (Farmer et al., 2011; Laidlaw
362 & Taylor, 2011; Yuen et al., 2012) indicate that the wide spread use of unleaded fuels has reduced but not

363 eliminated the anthropogenic sources of Pb related with motoring activities (e.g. additives in lubricants,
364 wear of vehicle components). Considering a potential chronic exposure through childhood, only sites 1
365 and 15 (Monsanto Park) have an estimated *HQ* that is below the threshold. Data from this type of
366 assessment indicates the potential health risks from the direct ingestion of dust borne Pb to children from
367 recreational areas in Lisbon. These results point out differences in risk estimates between exposure from
368 Pb in soil and outdoor dust. For soils and outdoor dusts of Lisbon the risk assessment study indicates that
369 (i) on average (i.e., a global *HQ* estimated for the area based on the average of the concentrations), the
370 estimated *HQ*s are more elevated for dusts; (ii) for individual assessments such as urban recreational areas
371 used by children, using soil or outdoor dust as exposure media results in different risk assessments (e.g.
372 dust at site 39 does not represent a health risk but soil raises some concern. Due to their different
373 characteristics both materials (soil and outdoor dusts) should probably be routinely included in surveys
374 that aim to assess exposure and health risk associated to the ingestion route.
375 A risk assessment study would ideally include all potential routes of exposure. However, in this study,
376 ingestion of soils/outdoor dusts is the only route considered since, at this time, chemical specific dermal
377 toxicity factors are not available although the EPA makes oral-to-dermal extrapolations for systemic
378 effects (US EPA, 2004). Other sources such as food and water ingestion were not considered as this is a
379 scenario-evaluation approach specific for children playing in outdoor recreational areas.
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389 Table2. Hazard Quotient (*HQ*) calculated for each age group and for the sum of the *ADI*s (represents potential
390 chronic exposure through childhood); some summary statistics (*n=19* soil samples); data in bold indicates values
391 above the safety level.

	HQ (age groups in years)			$HQ_{chronic}$
	1 - <3	3 - <6	6 - <12	Sum
1	0.32	0.34	0.24	0.90
5	0.92	0.97	0.69	**2.58**
6	0.30	0.31	0.22	0.84
8	0.29	0.31	0.22	0.83
11	0.05	0.05	0.04	0.14
14	0.31	0.33	0.24	0.88
15	0.04	0.04	0.03	0.11
16	0.36	0.38	0.27	1.01
18	0.62	0.66	0.47	**1.75**
27	0.46	0.49	0.35	**1.29**
30	0.32	0.34	0.24	0.90
31	0.66	0.70	0.50	**1.86**
33	**1.12**	**1.18**	0.85	**3.15**
39	**1.64**	**1.73**	**1.23**	**4.59**
40	0.95	1.01	0.72	**2.68**
42	0.73	0.77	0.55	**2.04**
43	0.76	0.80	0.57	**2.13**
44	0.23	0.24	0.17	0.65
47	1.03	1.09	0.78	**2.89**
Median	0.46	0.49	0.35	**1.29**
Mean	0.59	0.62	0.44	**1.64**

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394 Table3. Hazard Quotient (*HQ*) calculated for each age group and for the sum of the *ADI*s (potential chronic
395 exposure through childhood); some summary statistics (*n=8* dust samples); data in bold indicates values above the
396 safety level.

	HQ (age groups in years)			$HQ_{chronic}$
	1 - <3	3 - <6	6 - <12	Sum
1	0.28	0.29	0.21	0.78
5	0.59	0.62	0.44	**1.65**
15	0.09	0.10	0.07	0.26
18	0.53	0.56	0.40	**1.48**
30	0.99	1.05	0.75	**2.79**
33	0.75	0.80	0.57	**2.12**
39	0.74	0.78	0.56	**2.07**
47	**1.15**	**1.21**	0.86	**3.22**
Median	0.66	0.70	0.50	**1.86**
Mean	0.64	0.67	0.48	**1.80**

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398 4. Conclusions

399 The first study of Pb bioaccessibility in recreational areas of Lisbon, Portugal, assessing the risk from
400 dust and soil has identified the differences between the total and bioaccessible Pb concentrations and
401 hence the impacts on calculated *HQs* for the two host materials. Total and bioaccessible concentrations of
402 Pb are higher for outdoor dusts than for soils. Major fractions of Pb are in bioaccessible forms and the
403 values of *Bf* are higher compared to data reported in recent studies. The *Bf* of Pb in dusts is generally
404 higher than in soils, probably due to the finer grain size used for the dust samples. A negative correlation
405 between the *Bf* of Pb and the amount of carbonate minerals was found for soil samples with more than
406 20% of carbonate minerals. The amount of carbonates in the initial soil appears to be one factor
407 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 *HQs* 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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428 References

429 Agência Portuguesa do Ambiente, 2009. Atlas do Ambiente. http://sniamb.apambiente.pt/webatlas.
430 Accessed May 2009.

431 Bacigalupo, C., Hale, B., 2012. Human health risks of Pb and As exposure via consumption of home
432 garden vegetables and incidental soil and dust ingestion: A probabilistic screening tool. Sci. Total
433 Environ. 423, 27–38. DOI 10.1016/j.scitotenv.2012.01.057

434 Beauchemin, S., MacLean, L. C. W. & Rasmussen, P.E. (2011). Lead speciation in indoor dust: a case
435 study to assess old paint contribution in a Canadian urban house. Environ. Geochem. Health. 33, 343–
436 352. DOI: 10.1007/s10653-011-9380-8

437 Calabrese, E.J., Stanek, E.J., Barnes, R., 1996. Methodology to Estimate the Amount and Particle Size of
438 Soil Ingested by Children: Implications for Exposure Assessment at Waste Sites. Regul. Toxicol. Pharm.
439 24, 264–268.

440 Charlesworth, S., Everett, M., McCarthy, R., Ordóñez, A., de Miguel, E., 2003. A comparative study of
441 heavy metal concentration and distribution in deposited street dusts in a large and a small urban area:
442 Birmingham and Coventry, West Midlands, UK. Environ. Int. 29, 563–573. DOI 10.1016/S0160-
443 4120(03)00015-1

444 Costa, C., Reis, AP., Ferreira da Silva, E., Rocha F., Patinha, C., Dias, A.C., Sequeira, C., Terroso D.
445 (2012). Assessing the control exerted by soil mineralogy in the fixation of potentially harmful elements in
446 the urban soils of Lisbon, Portugal. Environ. Earth. Sci. 65, 1133-1145. DOI *10.1007/s12665-011-1362-8*

447 De Miguel, E., Iribarren, I., Chacón, E., Ordoñez, A., Charlesworth, S., 2007. Risk-based evaluation of
448 the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere. 66, 505–513.
449 DOI 10.1016/j.chemosphere.2006.05.065

450 Denys, S., Caboche, J., Tack, K., Rychen, G., Wragg, J., Cave, M., Jondreville, C., Feidt, C., 2012. In
451 Vivo Validation of the Unified BARGE Method to Assess the Bioaccessibility of Arsenic, Antimony,
452 Cadmium, and Lead in Soils. Environ. Sci. Technol. 46, 6252−6260.

453 Girouard, E., Zagury, G.J., 2009. Arsenic bioaccessibility in CCA-contaminated soils: Influence of soil
454 properties, arsenic fractionation, and particle-size fraction. Sci. Total Environ. 407, 2576-2585. DOI
455 10.1016/j.scitotenv.2008.12.019

456 Grøn, C., Andersen, L., 2003. Human bioaccessibility of heavy metals and PAH from soil. 840/2003.
457 Danish Environmental Protection Agency, Copenhagen.

458 Hu, X., Zhang, Y., Luo, J., Wang, T., Lian, H. & Ding, Z. (2011). Bioaccessibility and health risk of
459 arsenic, mercury and other metals in urban street dusts from a mega-city, Nanjing, China. Environ. Pollut.
460 159, 1215-1221. DOI 10.1016/j.envpol.2011.01.037

461 Farmer, J.G., Broadway, A., Cave, M.R., Wragg, J., Fordyce, F.M., Graham, M.C., Ngwenya, B.T.,
462 Bewley, R.J.F., 2011. A lead isotopic study of the human bioaccessibility of lead in urban soils from
463 Glasgow, Scotland. Sci. Total Environ. 409, 4958–4965. DOI 10.1016/j.scitotenv.2011.08.061

464 JECFA (1993). Evaluation of Certain Food Additives and Contaminants: 41st Report of the Joint
465 FAO/WHO Expert Committee on Food Additives. World Health Organization, Geneva (Technical
466 Reports Series No. 837).

467 JECFA (2011). Safety evaluation of certain food additives and contaminants: 73rd Report of the Joint
468 FAO/WHO Expert Committee on Food Additives. World Health Organization, Geneva (Technical
469 Reports Series No. 64).

470 Johnson, D. and Bretsch, J.K.., 2002. Soil lead and children's blood lead levels in Syracuse, NY, USA.
471 Environ. Geochem. Health. 24, 375–385.

472 Juhasz, A.L., Weber, J., Smith, E., 2011. Impact of soil particle size and bioaccessibility on children and
473 adult lead exposure in peri-urban contaminated soils. J. Hazard. Mater. 186, 1870–1879 DOI
474 10.1016/j.jhazmat.2010.12.095

475 Laidlaw, M.A.S. and Filippelli, G.M., 2008. Resuspension of urban soils as a persistent source of lead
476 poisoning in children: A review and new directions. Appl. Geochem. 23, 2021–2039. DOI
477 10.1016/j.apgeochem.2008.05.009

478 Laidlaw, M.A.S. and Taylor, M.P., 2011. Potential for childhood lead poisoning in the inner cities of
479 Australia due to exposure to lead in soil dust. Environ. Pollut. 159, 1-9. DOI
480 10.1016/j.envpol.2010.08.020

481 Landrigan, P.J., Sonawane, B., Butler, R.N., Transande, L., Callan, R., 2005. Early environmental origins
482 of neurodegenerative disease in later life. Environ. Health. Perspect. 113, 1230–1233. DOI:
483 10.1289/ehp.7571

Lanphear, B.P., Hornung, R., Khoury, J., Yolton, K., Baghurst, P., Bellinger, D.C., Canfield, R.L., Dietrich, K.N., Bornschein, R., Greene, T. et al. 2005. Low-Level Environmental Lead Exposure and Children's Intellectual Function: An International Pooled Analysis. Environ. Health. Perspect. 113, 894–899. DOI: 10.1289/ehp.7688

Li, X. and Huang, C., 2007. Environment impact of heavy metals on urban soil in the vicinity of industrial area of Baoji city, P.R. China. Environ. Geol. 52, 1631-1637. DOI 10.1007/s00254-006-0608-3

Ljung, K., Oomen, A., Duits, M., Selinus, O., Berglund, M.,2007. Bioaccessibility of metals in urban playground soils. J. Environ. Sci. Heal. A, 42, 1241–1250. DOI 10.1080/10934520701435684

Meunier L., Koch, I., Reimer, K.J., 2011. Effect of particle size on arsenic bioaccessibility in gold mine tailings of Nova Scotia. Sci. Total Environ. 409, 2233–2243. DOI 10.1016/j.scitotenv.2011.02.006

Morrison, D., Lin, Q., Wiehe, S., Liu, G., Rosenman, M., Fuller, T., Wang, J., Filippelli, G., 2012. Spatial relationships between lead sources and children's blood lead levels in the urban center of Indianapolis (USA). Environ. Geochem. Health. DOI 10.1007/s10653-012-9474-y

Morton-Bermea, O., Hernández-Álvarez, E., González-Hernández, G., Romero, F., Lozano, R. & Beramendi-Orosco, L.E., 2008. Assessment of heavy metal pollution in urban topsoils from the metropolitan area of Mexico City. J. Geochem. Explor. 101, 218–224. DOI 10.1016/j.gexplo.2008.07.002

Moya, J., Bearer, C.F., Etzel, R.A., 2004. Children's behavior and physiology and how it affects exposure to environmental contaminants. Pediatrics. 113, 996–1006.

Okorie, A., Entwistle, J., Dean J.R., 2011. The application of in vitro gastrointestinal extraction to assess oral bioaccessibility of potentially toxic elements from an urban recreational site. Appl. Geochem. 26, 789–796. DOI 10.1016/j.apgeochem.2011.01.036

Okorie, A., Entwistle, J., Dean J.R., 2012. Estimation of daily intake of potentially toxic elements from urban street dust and the role of oral bioaccessibility testing. Chemosphere, 86, 460–467. DOI 10.1016/j.chemosphere.2011.09.047

Oomen, A.G., Hack, A., Minekus, M., Zeijdner, E., Schoeters, G., Verstraete, W., Wiele, T.V.D., Wragg, J., Rompelberg, C.J.M., Sips, A.J.A.M., Wijnen, J.H.V.,2002. Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. Environ. Sci. Technol. 36, 3326-3334. DOI 10.1021/es010204v

512 Ottesen, R.T., Jan Alexander, J., Langedal, M., Haugland, T. & Høygaard, E. (2008). Soil pollution in
513 day-care centers and playgrounds in Norway: national action plan for mapping and remediation. Environ.
514 Geochem. Health. 30, 623-637. DOI 10.1007/s10653-008-9181-x

515 Patinha, C., Reis, A.P., Dias, C., Cachada, A., Adão, R., Martins, H., Ferreira da Silva, E., Sousa, A.J.,
516 2012. Lead availability in soils from Portugal's Centre Region with special reference to bioaccessibility.
517 Environ. Geochem. Health. 34:213–227. DOI 10.1007/s10653-011-9431-1

518 Reis, A.P., Patinha, C., Ferreira da Silva, E. and Sousa, A.J., 2012. Metal fractionation of cadmium, lead
519 and arsenic of geogenic origin in topsoils from the Marrancos gold mineralisation, northern Portugal.
520 Environ. Geochem. Health., 34:229–241. DOI 10.1007/s10653-011-9433-z

521 Rodriguez, R.R., Basta, N.T., Casteel, S.W., Pace, L.W., 1999. An in vitro gastrointestinal method to
522 estimate bioavailable arsenic in contaminated soils and solid media. Environ. Sci. Technol. 33, 642-649.
523 DOI 10.1021/es980631h

524 Ruby, M.V., Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., Mosby, D.E., Casteel, S.W.,
525 Berti, W., Carpenter, M., Edwards, D., Cragin, D., Chappell, W., 1999. Advances in evaluating the oral
526 bioavailability of inorganics in soil for use in human health risk assessment. Environ. Sci. Technol. 33,
527 3697-3705. DOI 10.1021/es990479z

528 Schumacher, B.A., 2002. Methods for the determination of Total Organic Carbon (TOC) in soils and
529 sediments. U.S. Environmental Protection Agency, Washington, DC; EPA/600/R-02/069 (NTIS PB2003-
530 100822).

531 Sheppard, S.C., Evenden, W.G.,1994. Contaminant enrichment and properties of soil adhering to skin. J.
532 Environ. Qual., 23, 604–613

533 U.S. Environmental Protection Agency (EPA), 1992. Guidelines for Exposure Assessment. U.S.
534 Environmental Protection Agency, Washington, DC, EPA/600/Z-92/001.

535 U.S. Environmental Protection Agency (EPA), 2007. Guidance for Evaluating the Oral Bioavailability of
536 Metals in Soils for Use in Human Health Risk Assessment. OSWER 9285.7-80.

537 U.S. Environmental Protection Agency (EPA), 2009. Highlights of the child-specific exposure factors
538 handbook. National Center for Environmental Assessment, Washington, DC; EPA/600/R-08/135.
539 Available from the National Technical Information Service, Springfield, VA and online at
540 http://www.epa.gov/ncea.

US Environmental Protection Agency (EPA), 2011. Exposure Factors Handbook: 2011 Edition. National Center for Environmental Assessment, Washington, DC; EPA/600/R-09/052F. Available from the National Technical Information Service, Springfield, VA, and online at http://www.epa.gov/ncea/efh.

Wragg, J., Cave, M. and Nathanail, P., 2007. A Study of the relationship between arsenic bioaccessibility and its solid-phase distribution in soils from Wellingborough, UK. J. Environ. Sci. Heal. A, 42: 1303–1315DOI 10.1080/10934520701436062

Wragg, J., Cave, M., Basta, N., Brandon, E., Casteel, S., Denys S., et al., 2011. An inter-laboratory trial of the unified BARGE bioaccessibility method for arsenic, cadmium and lead in soil. Sci. Total Environ. 409, 4016–4030. DOI 10.1016/j.scitotenv.2011.05.019

Yuen, J.Q., Olin, P.H., Lim, H.S., Benner, S.G., Sutherland, R.A., Ziegler, A.D. 2012. Accumulation of potentially toxic elements in road deposited sediments in residential and light industrial neighborhoods of Singapore. J.Environ. Manage.101, 151–163. DOI 10.1016/j.jenvman.2011.11.017

Zia, M.H., Codling, E.E., Scheckel, K.G., Chaney, R.L., 2011. In vitro and in vivo approaches for the measurement of oral bioavailability of lead (Pb) in contaminated soils: A review. Environ. Pollut. 159, 2320-2327. DOI 10.1016/j.envpol.2011.04.043.

http://www.cm-lisboa.pt. Accessed May 2009.