



Levels, sources and potential human health risks of organic pollutants in urban soils

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ABSTRACT

Urban soil quality may be severely affected by PAH and PCB contamination, impairing environmental and human health. A comprehensive study was conducted in two contrasting Portuguese urban areas (Lisbon and Viseu) in order to assess the levels of these contaminants and potential risks to human health, to identify sources and study their behavior in soils. The concentrations of PAHs and PCBs were related to the size of the city. The concentrations found in the larger city (Lisbon) were similar to other urban areas. Differences between profiles of the two urban areas were observed for both groups of contaminants, which could be attributed to differences of sources or climate. Lisbon seems to be affected by nearby sources (traffic, industry and incineration processes) whereas in the smaller city atmospheric transport may be playing an important role. Cluster analysis revealed that PAHs and PCBs were associated with anthropogenic toxic elements (Cu, Pb, Zn and Hg in Lisbon; Pb and Hg in Viseu), therefore reflecting common sources. It was also found that organic carbon was an important factor for PAHs and high chlorinated PCB retention in soils. The incremental probability of developing cancer over lifetime, based on a reasonable maximum exposure to PAHs present in Lisbon residential soils, was 9.0×10^{-6} and 2.4×10^{-6} for an occupational exposure, both slightly higher than the target risk of 1×10^{-6} . Similarly, the mutagenic risk of PAHs in Lisbon was 3.3×10^{-5} for residential soils and 1.8×10^{-6} in recreational areas.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are two groups of semi-volatile, chemically stable and hydrophobic organic compounds which are ubiquitous in the environment and good markers of urban activities (Fabietti et al., 2010; Ma et al., 2009; Zhang et al., 2007). PAHs are by-products resulting primarily from the incomplete combustion or pyrolysis of organic material, and therefore the origin could be either natural or anthropogenic. However, anthropogenic activities such as traffic, industry, domestic heating and incineration processes are major sources of these compounds. On the other hand, PCBs cannot be formed in nature and its usage is related with industry, even though nowadays their production is currently ceased. Yet, they are still present in many products (e.g. capacitors, transformers, hydraulic fluids, cutting oils, etc.) and they can also be formed as by-products of certain industrial processes or waste incineration (EA, 2007).

These organic pollutants (OPs) are primarily emitted to the atmosphere, and after their transport over short and long distances, in both gaseous and particulate forms, they accumulate in soils after dry and

wet atmospheric deposition (Heywood et al., 2006; Motelay-Massei et al., 2004; Ravindra et al., 2008). Consequently, the contamination of soils may result both from diffuse or point source contamination. The long range atmospheric transport turns these OPs into a trans-boundary environmental problem, reflected by their accumulation in soils all over the world, even at sites located far from human activity (Nam et al., 2009; Ravindra et al., 2008).

Once they reach the soils, OPs are likely to be strongly retained in the organic phase, due to their hydrophobicity and lipophilicity, and consequently, soil is the major sink for PAHs and PCBs (Srogi, 2007). Direct contact with soils contaminated with OPs may pose a risk to human health through its ingestion, dermal absorption and inhalation of particulates (Srogi, 2007; USEPA, 1991). Since some of these OPs are known or suspected of carcinogenic, mutagenic or endocrine disrupting properties, measuring the levels of these compounds in the environment is an important step to assess their potential hazard risk (CCME, 2010; USEPA, 2011).

The identification of contaminant sources is also a critical step in OP risk assessment and management, especially in complex environments such as urban areas, in which there is not a single source but several point and diffuse sources. For this reason, multivariate statistics or simple compound profiles and isomer ratios are normally used for source identification, even with some drawbacks (Cachada et al., 2009; Ravindra et al., 2008; Yunker et al., 2002). Specifically, for PAHs

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these approaches have been used to provide information on the possible origin (petrogenic versus pyrogenic origin) and sources of contamination (e.g.: tire debris, biomass or fuel combustion). The relationship between OP contamination and potentially toxic elements (PTEs) can also provide indications on their sources. Some studies reported that OP and PTE contamination can be related (Cachada et al., 2012; Maliszewska-Kordybach et al., 2009), but most studies on urban soil quality do not take into account both types of contaminants (Jiang et al., 2011; Peng et al., 2011; Wu et al., 2011). Soil properties are also often excluded from urban soil studies and as a consequence their role on OP fate in soils is not fully understood.

Due to the proximity of the population living in cities with urban soils, it becomes very important to assess their potential risks to human health. In the present study, the evaluation of the potential risks that OPs pose to human health was made by applying the USEPA risk assessment guidance for superfund (RAGS) methodology (USEPA, 1991). Therefore, the cancer incidence and the mutagenic risks for PAHs resulting from the exposure to urban soils during daily and recreational activities were calculated. Despite the several limitations (e.g. methodology may not reflect the Portuguese reality; low number of samples; high associated uncertainty) of this approach, it is an indication of the potential hazard.

This study intends to be a comprehensive study on OPs in urban soils, assessing the levels of these contaminants and potential risks to human health, identifying sources and studying their behavior. Thus, two contrasting Portuguese urban areas (Lisbon and Viseu, which differ in geological and climatic conditions, industrial and urban development processes) were studied (Fig. 1). The relationship between OPs (PAHs and PCBs) and between OP and PTE contamination was assessed, as well as the factors affecting their distribution (soil properties). Furthermore, a human health risk assessment was performed by calculating the cancer and mutagenic risks associated with different exposure routes and considering the different land uses of urban soils.

2. General characterization of the study areas

Lisbon city (Fig. 1a) is the largest urban area of Portugal, with a population of 547,631 inhabitants and an area of 85 km². The Lisbon metropolitan area is highly industrialized (petrochemical, chemical, textile, shipyard and metal processing industries), although most of the industry is located outside the urban area. A harbor and the

international airport are both located inside the urban area. In addition, several highways cross the city, with approximately 170,000 cars entering the city every day. The climate in the Lisbon region is temperate, with a daily mean temperature of 17.5 °C, being the temperature in the town center usually 2 °C higher, especially in summer. The total annual rainfall is 700 mm.

Viseu (Fig. 1b) is a small city with 47,250 inhabitants and the urban center has around 12 km². Industrial activities are present at a small scale, being the most important economic activities related with catering industry, wholesale and retail sectors. Regarding traffic, cars are the main transport used and the city is located nearby (around 3 km) one of the most important highways of the country. The climate in Viseu is characterized by high temperature extremes, with rigorous and wet winters and hot and dry summers. The daily mean temperature is 15 °C, and the total annual rainfall is 1400 mm.

3. Material and methods

3.1. Sampling and soil characterization

Fifty one composite samples were collected from Lisbon and fourteen from Viseu (0–10 cm). Samples from different land uses (ornamental gardens, parks, open spaces and roadsides) were collected and processed as described elsewhere (Cachada et al., in press; Cachada et al., 2012). Sampling location maps (Fig. 1) were produced with ArcGIS® Software (version 9.3).

The general characterization of soil samples included pH, organic matter content, cation exchange capacity and particle size distribution (Cachada et al., in press). In addition, organic carbon (OC) content, after elimination of carbonates with H₃PO₄ (Skalar Primac SCN for Lisbon soils and LECO CNHS-932 for Viseu soils) was also determined. The pseudo-total content of 8 PTEs (As, Co, Cr, Cu, Ni, Pb and Zn) and the total Hg concentrations were determined as previously described by Cachada et al. (in press).

3.2. Methodology for the determination of PAHs and PCBs

For extraction of PAHs and PCBs, 10 g of soil was Soxhlet extracted with 90 ml of hexane/acetone (2:1) for 8 h, at a rate of 10 cycles/h, in a prewashed glass fiber thimble (USEPA, 1996). The extracts were concentrated using a rotary evaporator (at 30 °C) and submitted to

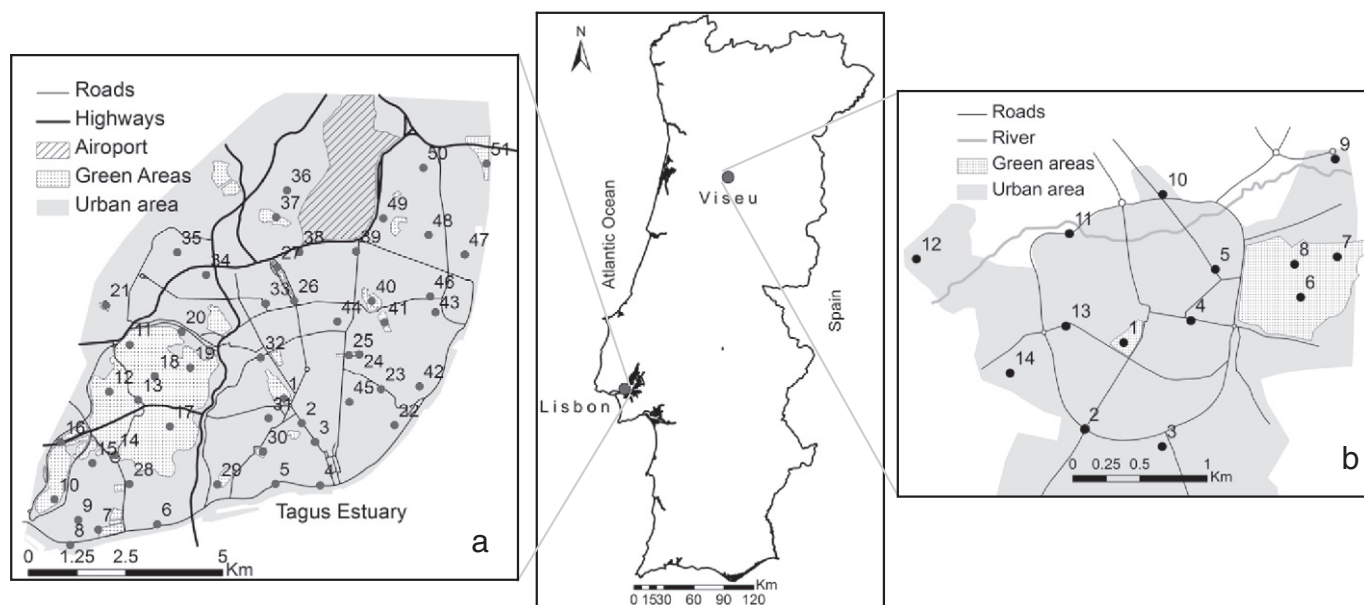


Fig. 1. Location of the cities and of the sampling sites in Lisbon (a) and Viseu (b).

a clean-up using solid-phase extraction cartridges filled with 1 g of silica (Supelclean® LC-Si), 2 g of neutral alumina (Supelclean® LC-AL-N), both 3% deactivated, and 0.5 g of Na₂SO₄ at the top. The elution was made with 20 ml of hexane/dichloromethane (9:1) and 10 ml of hexane/dichloromethane (2:1). The eluate was then concentrated down to 2 ml using a rotary evaporator, transferred to a vial and the volume was then reduced to approximately 0.1 ml under a gentle stream of pure nitrogen and solvent changed to dichloromethane for PAH analysis. For analysis of PCBs, the extracts were re-dissolved in hexane and further underwent a clean-up with 2 g of acidic silica (30% concentrated H₂SO₄, w/w), eluted with 15 ml of hexane and the solvent changed to isooctane before GC–MS analysis.

This study focused on the determination of 16 PAHs and 21 PCBs, based on both the USEPA and the Dutch lists. The 16 PAHs determined were acenaphthene (ACE), acenaphthylene (ACY), anthracene (ANT), benzo(a)anthracene (BAA), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(ghi)perylene (BGHI), benzo(a)pyrene (BAP), chrysene (CRY), dibenzo(ah)anthracene (DBAH), fluoranthene (FLA), fluorene (FLU), indeno(1,2,3-cd)pyrene (IND), naphthalene (NP), phenanthrene (PHE) and pyrene (PYR). The PCB congeners (1, 5, 18, 28, 31, 44, 52, 66, 87, 101, 110, 118, 138, 141, 151, 153, 170, 180, 183, 187 and 206) represent the common Arochlor formulations.

Extracts were analyzed using gas chromatography with mass spectrometry detection (GC/MS-QP5050A, Shimadzu Corporation), using helium as a carrier gas and a SPB-5 fused silica capillary column. The detection was achieved with a mass selective detector using electron ionization (EI) in the single ion monitoring mode (SIM). The injection volume was 1 µl and the splitless injection mode was used. The carrier gas flow was 1 ml/min for PAHs and 0.7 ml/min for PCBs. For the analysis of the 16 PAHs the injector temperature was 290 °C and the interface temperature was 300 °C. The oven temperature was programmed as follows: 40 °C for 2 min, increase at a rate of 10 °C/min until 220 °C, followed by 6 °C/min until 260 °C, and finally at 3 °C/min until 300 °C and kept for 6 min. For PCBs the injector temperature was 280 °C and the interface temperature was 300 °C. The oven temperature was programmed as follows: 40 °C for 2 min, increase at a rate of 10 °C/min until 290 °C and kept for 8 min.

3.3. Quality assurance and quality control (QA/QC) procedures

QA/QC procedures included replicates, procedure blanks and the analysis of certified reference materials. Replicate analysis of the soil samples gave an uncertainty <20% for each individual organic contaminant. Method blanks were used in every tenth sample in order to detect possible interferences from the reagents, glassware and other processing hardware, and results were always below the instrumental detection limit. Detection limits ranged from 0.15 to 0.63 µg kg⁻¹ for PAHs and from 0.02 to 0.14 µg kg⁻¹ for PCBs, depending on the specific compound. Recoveries of certified reference materials ranged from 90 ± 4 to 100 ± 2% for PCBs (LGC 6113) and from 78 ± 3 to 99 ± 4% for PAHs (RTC-CRM124-100). Internal standards, (decachlorobiphenyl for PCBs and a deuterated-PAH mixture for PAH determination), were added to samples before extraction and recoveries ranged from 60 to 109%.

3.4. Methodology used for human health risk assessment

The PAH toxic equivalent factors (TEFs) were used to calculate the toxic equivalents and quantify the PAH toxic potency of soil samples, expressed as BAP-equivalents (BAPEq) (Tsai et al., 2004). For PCBs, toxic equivalents were not calculated since only one of the PCBs analyzed (PCB118) has a TEF value attributed (USEPA, 2011).

Cancer and mutagenic risks associated with PAH and PCB exposure were based on the deterministic approach from USEPA RAGS methodology (USEPA, 1991). The potential exposure to the amount of OPs contained in soil was separately calculated for each route

(ingestion, dermal absorption and inhalation of particulates), as described in the USEPA screening level equations for preliminary remediation goals (USEPA, 2011), and presented in the electronic supplemental material (ESM). Cancer and mutagenic lifetime risks for ingestion and dermal adsorption were calculated by multiplying the predicted oral or dermal exposure by the chronic oral slope factor (CSF_o), since no dermal cancer slope factor has been established for these compounds. Regarding the inhalation of soil particles, risks were calculated by multiplying the exposure by the predicted chronic inhalation unit risk (IUR). The total lifetime carcinogenic and mutagenic risks were obtained by summing the individual risks calculated for the three exposure routes. Three types of land uses were considered for carcinogenic risk (residential, occupational, and recreational) and two for mutagenic risks (residential and recreational) (USEPA, 2011). All exposure parameters, including the age-dependent adjustment factor for mutagenic and carcinogenic risks, were selected according to the EPA's default values (Table S1 and Table S2; ESM). An exception was made for recreational land use, where it was considered an exposure frequency of 26 days and an exposure time of 2 h (Table S1). For residential and occupational exposure, risks were calculated for all sites, since they are all public areas and either inside or nearby residential areas. Risks associated with recreational sites were calculated only for parks and gardens, in which recreational activities are likely to occur. The exposure risks were calculated for different point estimates: mean, median, minimum, maximum concentrations, and for the 95% percentile of the upper confidence on the mean (UCL). The UCL (95%), along with the assumed exposure parameters, is considered a reasonable maximum exposure, according to USEPA (2011). For PAHs the risks were calculated based on the sum of BAPEq concentrations, and for PCBs as a sum of individual congeners (higher risk) (USEPA, 2011).

3.5. Statistical methods

Univariate statistical methods were initially performed to check the variability of the data and the presence of anomalies. Normality was tested (Shapiro-Wilk's test for normality, skewness and kurtosis values) and box-plots were also obtained. Since some parameters did not follow a normal distribution, Spearman correlations were used to test the relationships between variables.

In cases where the compounds were present below the detection limit, missing values were considered as equal to one tenth of the detection limit. This value was chosen in order to minimize an over-estimation of samples with many PCB congeners below the detection limit. This is a relevant issue in the present study because levels found in some of the samples are low and very close to the detection limit.

Cluster analysis (CA) was performed in order to classify similar observations into groups, following an agglomerative hierarchical clustering method (Ward method with Euclidean distances). CA included data on general parameters (pH, OC and clay particle size), since the parent material is a very important factor that will influence the natural concentrations and the soil properties. Since these statistical methods are severely affected by the data distribution and the presence of outliers, a log transformation was performed. Furthermore, the data was standardized to avoid the effects resulting from differences in units of measure.

The 95% UCL used for risk assessment analysis was calculated non-parametrically using the statistical package ProUCL® available by USEPA. Other descriptive and multivariate statistical analyses (Spearman correlations, CA) were performed in SPSS®.

4. Results and discussion

4.1. Levels and sources of PAHs in urban areas

Concentrations of the Σ16PAHs obtained in surface soils of both cities are presented in Fig. 2a and Table 1. The accumulation of PAHs

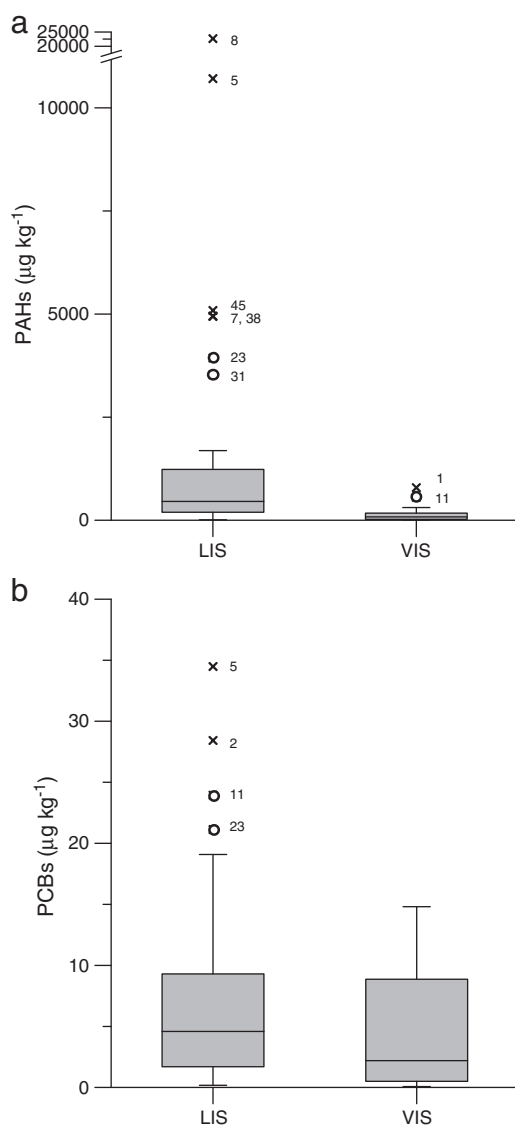


Fig. 2. Box-plots showing the variation of PAH (a) and PCB (b) concentrations in Lisbon (LIS) and Viseu (VIS). Boxes define the interquartile range and the line is the median. Outliers are defined as values between 1.5 and 3 box lengths (O) and extreme values as more than 3 box lengths (x).

in urban soils over many years and the presence of more sources explains the higher concentrations measured in larger and industrialized cities like Lisbon in contrast to other Portuguese cities (Table 1) like Viseu and Estarreja (around 5 times lower median than in Lisbon). The mean concentration and maximum values observed in Lisbon were comparable or even higher than the ones observed in other studies with the exception of Glasgow, which reflects the presence of important hotspots, as observed in Fig. 2a. When comparing median concentrations with cities from all over the world (Table 1), Lisbon soils showed lower levels than European cities, but generally higher than the ones found in Asian cities. Higher concentrations in European urban areas were observed by other authors (Liu et al., 2010a; Wilcke, 2007; Zhang et al., 2007) and a similar trend was also observed for global background soils (Nam et al., 2009), in which climate was the main reason pointed out for this difference.

The fairly short history of the city of Viseu, the recent growth in population, the size of its urban area and the lack of major industrial activity (with subsequently less fossil fuel combustion), explain the low concentrations measured. For example, Estarreja, which is a very small Portuguese town, presents slightly higher contamination levels

of PAHs due to the presence of industry and nearby busy roads (Cachada et al., 2012). Median concentration found in Viseu was lower than that in Swiss soils ($163 \mu\text{g kg}^{-1}$), unpolluted soils from Spain ($242 \mu\text{g kg}^{-1}$), natural and agricultural soils ($<250 \mu\text{g kg}^{-1}$) from Italy and Poland, or to the background ($136 \mu\text{g kg}^{-1}$) referred for Europe (Fabiatti et al., 2010; Maliszewska-Kordybach et al., 2009; Desaulles et al., 2008; Nadal et al., 2007; Nam et al., 2009).

In Lisbon soils, high PAH concentrations (Fig. 2a) were observed in historical parks and gardens essentially located in the city center (samples 5, 7, 8, 23, 31 and 45; Fig. 1a). This area is close to the river and it is the oldest part of the city, having a high population density. In Viseu, the highest concentration observed (Fig. 2a) was also in a historical park at the city center (sample 1; Fig. 1b). Historical sites are especially important when tracing urban diffuse contamination, as a result of long-term exposure to contaminants leading to an accumulation in soil's upper layer (Liu et al., 2010a; Zhang et al., 2007). As a result, these soils are usually multi-contaminated as observed in both cities studied, since some of the outlier values observed for PAHs coincide with the ones of PCBs (Fig. 2b) and PTEs (samples 5, 7, 31 in Lisbon and sample 1 in Viseu) (Cachada et al., in press).

In the past, the oldest area of Lisbon was very industrialized, but nowadays mobile sources such as roadway traffic, aircraft and shipping are probably most important. Samples 5, 7 and 8 (Fig. 1a) are all very close to a busy road and a railway line; another outlier value was observed near the airport and an important highway (sample 38). However, other important PAH sources should be considered (Ravindra et al., 2008): samples 7 and 8 are also located nearby the docks; sample 5, in addition to being close to the most important dock, it is also close to a shipyard industry; sample 23 is located near a crematorium; and sample 38 is very close to the only incinerator of hospital waste in Portugal.

In Viseu, none specific point source could be identified. The major sources of PAHs in Viseu are, in fact, likely to be diffuse sources such as wood and coal combustion (domestic heating, nearby agriculture, forest fires) and diesel engines from domestic heating and from the nearby highway, which is the most important in the country regarding freight. The great contribution of low temperature sources in Viseu compared to Lisbon, in which there is a great input of high temperature industrial combustion, seems to be reflected in the PAH profiles, since Viseu shows a slightly higher median of percentages of low molecular weight (LMW) PAHs (Fig. 3a, Fig. S1) (Boonyatumanond et al., 2007; Ravindra et al., 2008; Wilcke, 2007). These compounds are normally present in gaseous form and they are related with ubiquitous atmospherically dispersed emissions, being subjected to longer distance transport (Wilcke, 2007). Climate may, therefore, play a role in this difference of profiles, since the higher levels of precipitation and lower temperatures observed in Viseu may enhance wet deposition process and condensation, respectively (Desaulles et al., 2008). On the other hand the higher temperatures observed in Lisbon can strongly affect the degradation and volatilization of LMW PAHs (Nadal et al., 2004).

The high molecular weight (HMW) PAHs (≥ 4 rings) are dominant in the two cities studied (Fig. 3a, Fig. S1). This predominance is typical in urban areas and may be due to (i) the higher persistence of these compounds in soils, (ii) the predominance of combustion over petrogenic sources, and (iii) the tendency of HMW PAHs to accumulate in soils that are close to emission sources (Chung et al., 2007; Liu et al., 2010b; Morillo et al., 2007). The most abundant PAHs found in both cities, and especially in Lisbon, were FLA and PYR (Fig. 3a), compounds that are usually associated with fossil fuel (especially diesel), coal and biomass combustion, but also with tire debris (Boonyatumanond et al., 2007; Ravindra et al., 2008). The high contribution of BGHI is related with vehicle emissions (especially light-duty), and the greater contribution of IND in Lisbon can be associated, in addition to traffic, with oil combustion or industrial sources (Boonyatumanond et al., 2007; Oliveira et al., 2011; Ravindra et al., 2008). Yet, using these

Table 1Median, mean concentration and range of OPs ($\mu\text{g kg}^{-1}$) in urban soils around the world.

	No. inhab.	ΣPAHs				ΣPCBs				Ref.
		Median	Mean	Min	Max	Median	Mean	Min	Max	
Lisbon, Portugal	564,567	456	1544	6.3	22,670	4.6 ^b	7.0 ^b	0.18 ^b	34 ^b	This study
Viseu, Portugal	47,250	83	169	6.0	790	2.3 ^c	4.1 ^c	0.06 ^c	18 ^c	This study
Estarreja, Portugal	7000	98	–	27	2016	0.76 ^c	1.7 ^c	0.08 ^c	6.8 ^c	
Aveiro, Portugal	73,500	–	–	–	–	8.8 ^d	–	2.3 ^d	55 ^d	Cachada et al., 2012
						7.9 ^d	–	0.62 ^d	73 ^d	Cachada et al., 2009
Glasgow, Scotland	600,000	8337 ^a	11,930 ^a	1487 ^a	51,822 ^a	2.6 ^e	–	0.15	41	
						9.4 ^e	–	4.5 ^d	78 ^d	Cachada et al., 2009; Morillo et al., 2007
Torino, Italy	900,000	704 ^a	1990 ^a	148 ^a	23,500 ^a	14 ^d	–	1.9 ^e	43 ^e	
						6.6 ^e	–	1.8 ^d	172 ^d	Cachada et al., 2009; Morillo et al., 2007
Ljubljana, Slovenia	300,000	791 ^a	989 ^a	218 ^a	4488 ^a	6.8 ^d	–	0.72 ^e	86 ^e	
						2.1 ^e	–	2.8 ^d	48 ^d	Cachada et al., 2009; Morillo et al., 2007
Uppsala, Sweden	136,500	–	–	–	–	0.67 ^e	–	0.67 ^e	29 ^e	
						5.7 ^d	–	2.3 ^d	77 ^d	Cachada et al., 2009
						2.3 ^e	–	0.54 ^e	47 ^e	
Terragona, Spain	155,000	–	438	42	1472	–	4.4 ^c	0.19 ^c	10 ^c	Nadal et al., 2007
Beijing, China	18000,000	688	1228	93	13,141	13 ^f	12 ^f	nd ^{fg}	37 ^f	Peng et al., 2011
						3.2 ^g	3.1 ^g	–	9.3 ^g	Wu et al., 2011
Shangai, China	20600,000	314	1700	62	31,900	–	3.1 ^h	0.23 ^h	11 ^h	Liu et al., 2010b;
										Jiang et al., 2011
Hong Kong	6800,000	140	–	ND	19,500	3.9 ^c	4.8 ^c	1.6 ^c	9.9 ^c	Chung et al. 2007; Zhang et al., 2007
Harbin, China	3800,000	301	837	202	3256	2.1 ⁱ	2.2 ⁱ	0.53 ⁱ	6.2 ⁱ	Ma et al., 2009
						0.47 ^c	0.53 ^c	0.19 ^c	1.2 ^c	

ND = not detected.

^a $\Sigma 15\text{PAHs}$.^b $\Sigma 21\text{PCBs}$.^c $\Sigma 7\text{indicatorsPCBs}$.^d $\Sigma 19\text{PCBs}$.^e $\Sigma 5\text{indicatorsPCBs}$.^f $\Sigma 18\text{PCBs}$.^g $\Sigma 6\text{indicatorsPCBs}$.^h $\Sigma 74\text{PCBs}$.ⁱ $\Sigma 44\text{PCBs}$.

composition patterns to trace the sources in urban areas is very difficult due to the presence of mixed sources and because PAH composition profiles can be weathered (Brandli et al., 2008; Katsoyiannis et al., 2011; Zhang et al., 2005). The use of isomer ratios of selected pairs of isomers (Table S3) has been widely applied in order to overcome these constraints. However, it was not possible to address specific sources in the present study, since different ratios pointed to different results as observed by other studies (Brandli et al., 2008; Katsoyiannis et al., 2011). Even when applying the correction factors for soils indicated by Zhang et al. (2005), as suggested in the study of Brandli et al. (2008), the conclusions remain similar.

4.2. Levels and sources of PCBs in urban areas

Concentrations of the $\Sigma 21\text{PCBs}$ obtained in surface soils of both cities are presented in Fig. 2b. Table 1 shows, in addition to the results for $\Sigma 21\text{PCBs}$, the sum of concentrations of the 7 indicators ($\Sigma 7\text{indicatorsPCBs}$). The variability of results found in the present study is very high, with some samples showing relatively high concentrations (even in Viseu), as observed in other cities around the world (Table 1). The concentrations observed in the Lisbon urban area were not very high, and comparable to the ones found in other smaller cities like Ljubljana, Uppsala and Tarragona. In bigger and very industrialized cities, like Torino and Glasgow, much higher concentrations were observed. However, these levels were similar or even higher than the ones found in Asian cities (Table 1), and the reason should be the same given for PAHs. Median concentration of PCBs in Lisbon was lower than in Aveiro and Estarreja soils, which are chemical smaller Portuguese cities, but likely to be affected by a nearby chemical complex and a pulp and paper mill (Cachada et al., 2009; Cachada et al., 2012).

Mean concentration of PCBs in Viseu is somewhat high, only slightly lower than Lisbon's value. Concentrations of PCBs in Viseu

were higher than those measured in unpolluted soils from Spain ($\Sigma 7\text{PCBs}$ with a mean of $0.77 \mu\text{g kg}^{-1}$), close to the values in natural soils from Italy and British soils ($\Sigma 32\text{PCBs}$ with a mean of $3.5 \mu\text{g kg}^{-1}$ and $5.0 \mu\text{g kg}^{-1}$, respectively) but lower than Switzerland soils ($\Sigma 7\text{PCBs}$ with a median of $1.6 \mu\text{g kg}^{-1}$) (Desaules et al., 2008; Fabietti et al., 2010; Heywood et al., 2006; Nadal et al., 2007).

Only Lisbon showed outlier values (Fig. 1b), three of them in the city center and within those, two are historical sites (5 and 23), as observed for PAHs. In addition, sample 5 is very close to the shipyard industry where PCBs were widely used (e.g. paints, coatings), and sample 23 is located near the crematorium (PCBs may be released due to their presence in materials, precursors and chlorine in the cadavers and in some co-combusted plastics). Other specific hotspots may be due to the introduction of contaminated foreign soil or due to the use of contaminated sewage sludge as a fertilizer, such as the case of sample 2, which is a recent flowerbed in the city center. Accidental spill or improper waste disposal may also be a source of PCBs, as the case of sample 11 since this sample was located in a forest area inside a park and no other specific source could be addressed. Sample 38, despite not being considered an outlier, is very important since it shows high PCB concentration ($19 \mu\text{g kg}^{-1}$) and it is close to the incinerator of hospital waste, which may be a source of PCBs.

In Viseu, high PCB concentrations were observed in sample 6, located in a forest area inside a park and therefore the reason could be an accidental spill or improper waste disposal; and in sample 13, which is a recent residential area, in which new soil is likely to have been introduced. Since no other specific sources are likely to be present, the most probable origin of PCBs in Viseu soils is atmospheric transport from other contaminated areas. The slightly higher contribution of lower chlorinated PCBs ($\leq 4\text{Cl}$) in Viseu when compared to Lisbon (Fig. 3b, Fig S2), may not only be a consequence of

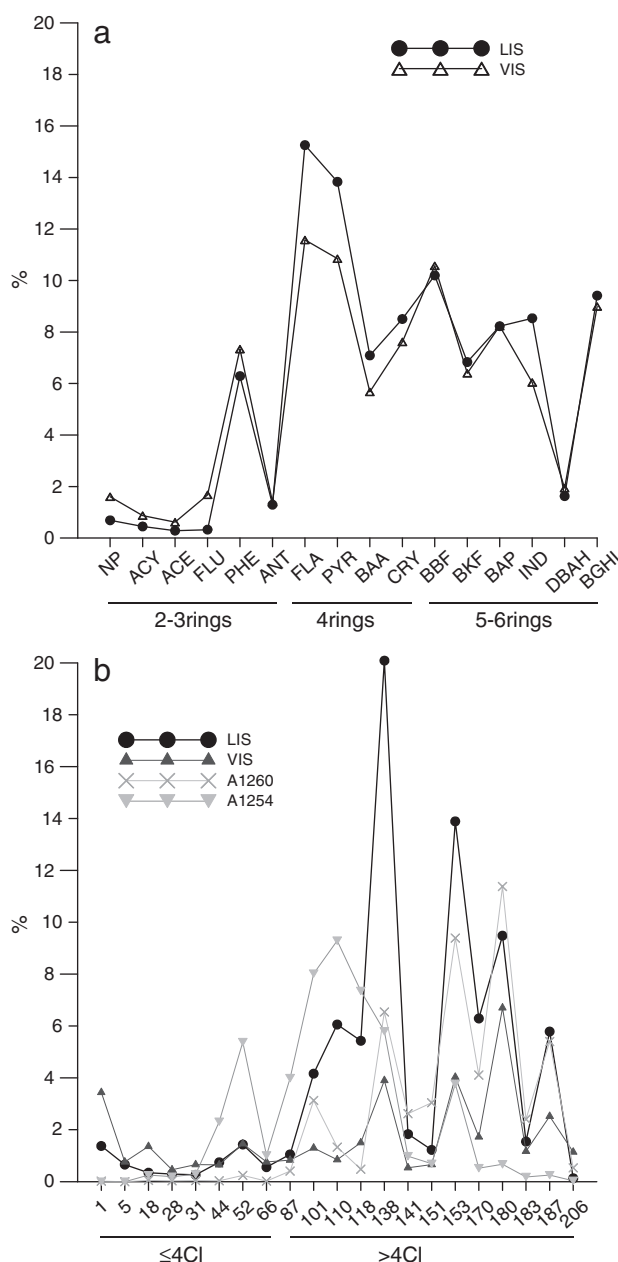


Fig. 3. Median percentage of individual compounds of PAHs (a) and PCBs (b) observed for the two cities. For PCBs, the percentage of compounds present in Arachlor 1260 (A1260) and Arachlor 1254 (A1254) is also shown.

long-range atmospheric transport but also of climate differences, as referred for PAHs (Motelay-Massei et al., 2004; Zhang et al., 2007). Nevertheless, lower-chlorinated PCBs are present in lower percentages than the higher chlorinated ones ($>4\text{Cl}$), especially in Lisbon (Fig. 3b). In both cities the most abundant congeners were PCBs 138, 153 and 180 (Fig. 3b), and similar to results observed in other European cities, in British soils and in unpolluted soils from Spain (Cachada et al., 2009; Heywood et al., 2006; Nadal et al., 2007). Overall, the profiles from both cities were similar to those observed in other cities, including other Portuguese cities, where it was found that the profiles resemble Arachlor 1260 (Cachada et al., 2009; Cachada et al., 2012). Similar findings can be addressed for the present study, especially for Viseu, yet Lisbon PCB profiles also show some similarity with Arachlor 1254 (Fig. 3b). Moreover, the high contribution of high chlorinated PCBs (HC-PCBs) in this city can also

be attributed to the presence of nearby high temperature sources (e.g. incineration).

4.3. Controlling factors and relationship among contaminants

Soil properties and PTE concentrations can be found in the ESM (Tables S4 and S5). The dendrogram of CA was similar in both cities, showing three major groups (Fig. 4). In both cases it was observed a group formed by PTEs which included the elements considered from telluric origin (Co, Cr and Ni) (Cachada et al., in press). Another group, also observed in both cities, is formed by OPs, anthropogenic PTEs (Cu, Pb, Zn and Hg in Lisbon; Pb and Hg in Viseu) and OC (Fig. 4). Therefore, this cluster can be related to a common anthropogenic source or may be governed by the OC relationships, since these elements are normally strongly associated with soil organic matter. In order to investigate whether the relationships observed between OPs and anthropogenic PTEs were due to common source or if they might be affected by soil properties, the data were normalized for the OC content. The CA remains similar after data normalization for both cities (data not shown), however some correlations changed indicating that OC may affect the relationships observed (Tables S6 and S7).

After normalization, PAHs were still positively correlated with PCBs in Lisbon soils (Table S7), although this correlation was stronger for the HC-PCBs ($\rho = 0.568$, $p < 0.01$). Similarly, correlations between PTEs and PCBs were low (Table S7), but stronger when looking only for HC-PCBs (≥ 0.410 , $p < 0.05$). Since the presence of HC-PCBs can be attributed to the presence of nearby high temperature sources, its relationship with PAHs and PTEs may indicate the presence of common sources such as industry or incineration, as observed in other studies conducted in impacted areas (Cachada et al., 2012). In Viseu, no correlations were observed after normalization between PCBs and other contaminants, indicating distinct sources of these compounds.

PAHs have been found to coexist with PTEs due to similar sources, such as motor vehicle emissions (Cachada et al., 2012; Maliszewska-Kordybach et al., 2009). The present study confirms this association, especially between PAHs, Pb and Hg in both cities, with correlations higher than 0.767 ($p < 0.01$; Table S7) even after OC normalization. In addition, significant correlations ($p < 0.01$; Table S7) were also observed for the other two urban elements in Lisbon soils (Cu, Zn), suggesting common sources, such as traffic.

In both cities correlations with OC were similar for LMW and HMW PAHs, although slightly higher for the second group. Stronger correlations between HMW PAHs and OC had been already observed, especially in more contaminated areas, and they can be related with their lower mobility and the fact that they are normally associated with particles and, therefore, tend to deposit near the sources (Brandli et al., 2008; Maliszewska-Kordybach et al., 2009).

For PCBs, a significant correlation with OC was observed for HC-PCBs ($\rho = 0.618$, $p < 0.01$) in Lisbon soils. Similar observations were found in British soils (Heywood et al., 2006), in Swiss soils (Brandli et al., 2008) and in urban soils from Torino (Cachada et al., 2009). These positive correlations between OC and soil PCBs have been addressed to the concept of “hopping” (compounds that undergo a series of emission–deposition cycles that lead to accumulation in soils enriched in OC) (Heywood et al., 2006). Even though it is generally accepted that OC is a sorbent of PCBs (Ma et al., 2009; Zhang et al., 2007), many studies did not found any relation as observed for Viseu (Cachada et al., 2009; Jiang et al., 2009; Liu et al., 2010b).

Correlations were stronger between organic carbon and PCBs than with PAHs in Lisbon soils, reflecting the stronger binding of the first group to soils as observed in other studies (Desaules et al., 2008; Heywood et al., 2006). However, different results were observed in Viseu. This ambiguity has been already reported (Desaules et al., 2008; Zhang et al., 2007) highlighting that the fate of OPs in the environment may be highly variable and that there is a lack of understanding of controlling factors, especially in urban soils.

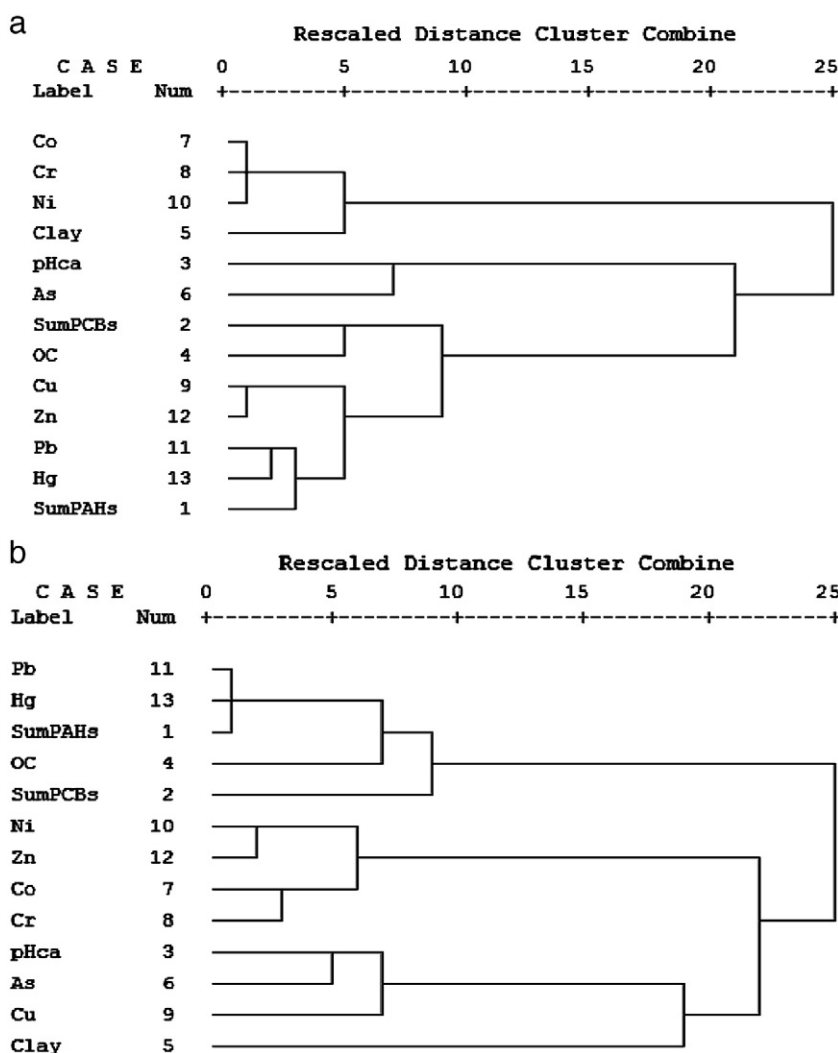


Fig. 4. Dendrogram of the cluster analysis of OPs, PTEs and general parameters for Lisbon (a) and Viseu (b) soils.

4.4. Risk assessment of OPs in urban areas

Twenty percent of Lisbon samples were above target value from the Dutch guidelines (VROM, 2000), and 13% were above the guideline values for soil quality criteria based on both chronic and ecotoxicological effects recommended by Danish EPA (DEPA, 2002). Taking into consideration the concentrations recommended by Danish EPA for BAP and DBAH, 27% of soils were above for the former and 10% for the latter. Regarding Canadian soil guidelines for the protection of environmental health in residential areas (CCME, 2010), only 2 samples showed values above the guidelines. No Lisbon sample showed concentrations above the guideline values established for PCBs (CCME, 2007; VROM, 2000). All samples from Viseu were below the guideline values for both PAHs and PCBs.

The risk-based soil criterion for protection of human health from Canada, based on PAH carcinogenic effect (CCME, 2010), indicates a safe level of $600 \mu\text{g BAPEq kg}^{-1}$. Only 4 samples from Lisbon showed concentrations above this value (1729, 3416, 761, and $645 \mu\text{g BAPEq kg}^{-1}$ for samples 5, 8, 38, and 45, respectively). The ΣBAPEq (mean value) in Lisbon was $229 \mu\text{g BAPEq kg}^{-1}$ and in Viseu $24 \mu\text{g BAPEq kg}^{-1}$ (Table S8). Levels observed for Lisbon are lower than the ones found in Shanghai ($428 \mu\text{g BAPEq kg}^{-1}$) but higher than levels found in Beijing ($181 \mu\text{g BAPEq kg}^{-1}$) and in Tarragona ($124 \mu\text{g BAPEq kg}^{-1}$) (Jiang et al., 2009; Liu et al., 2010a; Nadal et al., 2004).

Risk assessment results for residential exposure to PAHs and PCBs are shown in Table 2. Regarding cancer risks, PAH was the group of contaminants showing the highest reasonable maximum exposures in both cities, given by the UCL (95%). The most contaminated site in Lisbon represents a risk of 5.5×10^{-5} and in Viseu the maximum value rises to 2.1×10^{-6} . Mutagenic risks of PAHs are higher than cancer risks (Table 2), being the reasonable maximum exposure of 3.3×10^{-5} for Lisbon and 3.2×10^{-6} for Viseu. These values are higher than the target excess individual lifetime risk, which is one-in-one-million (10^{-6}) (USEPA, 2011). For PCBs, cancer risks were always below the target level. For all contaminants and in both cities, the highest risks were found to be from the ingestion exposure route, followed by dermal (always within one order of magnitude) and, at a very low level, the inhalation exposure. Comparing with other studies, Lisbon showed slightly higher total risks for BAPEq than the ones found in Tarragona or in Beijing (for normal conditions) (Nadal et al., 2011; Peng et al., 2011). The total risk for PCBs is similar for the two cities and also similar to that found in Tarragona (Nadal et al., 2011).

For adults, the cancer risks were calculated for occupational land use (outside workers, e.g. gardeners). Only PAH levels in Lisbon may represent some concern (Table S9), being the UCL (95%) of 2.4×10^{-6} and the maximum value observed 1.5×10^{-5} . In recreational areas, cancer and mutagenic risks were calculated only for PAHs (Table S10), since for other compounds the potential risk should be negligible due to low concentrations. The cancer risk for

Table 2

Concentrations of OPs (Cs) and results for ingestion (Ing), dermal (Derm), inhalation (Inh) and total cancer risks for residential land use, in both cities. Mutagenic risks of PAHs are also shown.

	Lisbon					Viseu				
	Cs ($\mu\text{g kg}^{-1}$)	Ing	Derm	Inh	Total	Cs ($\mu\text{g kg}^{-1}$)	Ing	Derm	Inh	Total
<i>PAHs – cancer</i>										
Mean	229	2.6E-6	1.1E-6	7.6E-11	3.7E-6	24	2.8E-07	1.1E-07	8.1E-12	3.9E-07
Med	61	6.9E-7	2.9E-7	2.0E-11	9.8E-7	11	1.3E-7	5.3E-8	3.8E-12	1.8E-07
Min	0.18	2.1E-9	8.7E-10	6.1E-14	3.0E-9	0.6	7.2E-09	3.0E-09	2.1E-13	1.0E-08
Max	3416	3.9E-05	1.6E-05	1.1E-09	5.5E-05	127	1.5E-06	6.0E-07	4.2E-11	2.1E-06
UCL (95%)	558	6.4E-06	2.6E-06	1.9E-10	9.0E-06	47	5.4E-07	2.2E-07	1.6E-11	7.6E-07
<i>PCBs – cancer</i>										
Mean	7.0	2.2E-08	9.7E-09	1.2E-12	3.2E-08	4.6	1.4E-08	6.4E-09	7.7E-13	2.1E-08
Med	4.7	1.5 E-08	6.5E-09	8.1E-13	2.1E-08	2.2	7.0E-09	3.1E-09	3.8E-13	1.0E-08
Min	0.25	7.8E-10	3.5E-10	4.3E-14	1.1E-09	0.19	5.8E-10	2.6E-10	3.1E-14	8.4E-10
Max	35	1.1E-07	4.8E-08	5.9E-12	1.6E-07	15	4.6E-08	2.1E-08	2.5E-12	6.7E-08
UCL (95%)	9.0	2.8E-08	1.2E-08	1.5E-12	4.0E-08	8.5	2.6E-08	1.2E-08	1.4E-12	3.8E-08
<i>PAHs – mutagenic</i>										
Mean	229	9.4E-06	4.3E-06	1.9E-10	1.4E-05	24	1.2E-06	4.6E-07	2.0E-11	1.6E-06
Med	61	2.5E-06	1.1E-06	5.1E-11	3.6E-06	11	5.5E-07	2.1E-07	9.5E-12	7.7E-07
Min	0.18	7.5E-09	3.5E-09	1.6E-13	1.1E-08	0.6	3.1E-08	1.2E-08	5.3E-13	4.3E-08
Max	3416	1.4E-04	6.4E-05	2.9E-09	2.0E-04	127	6.2E-06	2.4E-06	1.1E-10	8.6E-06
UCL (95%)	558	2.3E-05	1.0E-05	4.7E-10	3.3E-05	47	2.3E-06	8.8E-07	4.0E-11	3.2E-06

the more contaminated local, which is in fact a recreational area, was 4.1×10^{-6} and the UCL (95%) was 4.3×10^{-7} . However, mutagenic risks are higher, with the most contaminated site representing a risk of 1.2×10^{-5} , whereas the UCL (95%) is 1.3×10^{-6} . For Viseu, risks were always below 10^{-6} .

These results indicate that the total lifetime carcinogenic or mutagenic risk of PAHs in Lisbon may represent some concern, especially for residential and occupational land use. Indeed, PAH contamination in Lisbon requires more attention and further work should be done, such as the use of a larger dataset (which may be important due to the high variability of results) and other approaches to characterize risks (e.g. probabilistic approach in order to evaluate variability and uncertainty). This will provide a more substantiated overview of PAH risks in Lisbon urban soils.

5. Conclusions

In general, concentrations of OPs in Lisbon were high (mean value of $1544 \mu\text{g kg}^{-1}$ for PAHs and $7.0 \mu\text{g kg}^{-1}$ for PCBs), whereas in Viseu they were low (mean value of $169 \mu\text{g kg}^{-1}$ for PAHs and $4.6 \mu\text{g kg}^{-1}$ for PCBs), when compared with other urban areas. The great variability of the results observed might be a result not only of the proximity to sources, source type, age of sites (time for cumulative deposition) but also of the retention capacity of soil. The reason for the lower concentrations of OPs measured in Viseu is likely to be the size of the town and the lack of major industrial activity. Nevertheless, levels of PCBs in this town were not as low as expected and atmospheric transport should be the main reason. This hypothesis is supported by the differences observed in the OP profile of the two cities. Even so, differences in climate should be considered. Traffic, domestic heating, agriculture practices and forest fires may also be a source of PAHs into Viseu urban soils. Whereas in Lisbon, local high temperature sources of OPs such as industry and incineration or traffic are more important, as observed also by their relationship with PTEs. The influence of OC on the retention of OPs is still not very clear; nevertheless, it was observed in present study that OC affects the fate of PAHs in both cities and of HC-PCBs in Lisbon soils.

Only the Lisbon samples showed PAH values above guidelines. Moreover, the reasonable maximum exposure to PAH contamination in residential soils is slightly higher than the target excess individual lifetime cancer risk, and the mutagenic risk is even higher. Viseu, in

spite of the low contamination levels, showed mutagenic risks of PAHs very close to the target value. Similarly, the cancer risks of PAHs in Lisbon for an occupational exposure, as well as the mutagenic risks in recreational areas, are at the target level. PCB risks were below the levels of concern, with similar values in the two cities.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2012.04.075>.

References

- Boonyatumanond R, Murakami M, Wattayakorn G, Togo A, Takada H. Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. *Sci Total Environ* 2007;384:420–32.
- Brandli RC, Bucheli TD, Ammann S, Desaulles A, Keller A, Blum F, et al. Critical evaluation of PAH source apportionment tools using data from the Swiss soil monitoring network. *J Environ Monit* 2008;10:1278–86.
- Cachada A, Dias A, Pato P, Mieirol C, Rocha-Santos T, Pereira M, et al. Major inputs and mobility of potentially toxic elements contamination in urban areas. *Environ Monit Assess* in press: 1–16. <http://dx.doi.org/10.1007/s10661-012-2553-9>.
- Cachada A, Lopes L, Hursthouse A, Biasioli M, Grcman H, Otabbong E, et al. The variability of polychlorinated biphenyls levels in urban soils from five European cities. *Environ Pollut* 2009;157:511–8.
- Cachada A, Pereira M, Ferreira da Silva E, Duarte A. Sources of potentially toxic elements and organic pollutants in an urban area subjected to an industrial impact. *Environ Monit Assess* 2012;184:15–32.
- CCME (Canadian Council of Ministers of the Environment). Summary tables. Update 7.0. Canadian soil quality guidelines for the protection of environmental and human health. Canadian soil quality guidelines; 2007. <http://ceqg-rcqe.ccm.ca/>.
- CCME (Canadian Council of Ministers of the Environment). Polycyclic aromatic hydrocarbons. Canadian soil quality guidelines for protection of environmental and human health. Canadian soil quality guidelines; 2010. <http://ceqg-rcqe.ccm.ca/>.
- Chung MK, Hu R, Cheung KC, Wong MH. Pollutants in hong kong soils: polycyclic aromatic hydrocarbons. *Chemosphere* 2007;67:464–73.

- DEPA (Danish Environmental Protection Agency). Guidelines on remediation of contaminated sites. Environmental guidelines no. 7. Danish Ministry of Environment; 2002.
- Desaules A, Ammann S, Blum F, Brandli RC, Bucheli TD, Keller A. PAH and PCB in soils of Switzerland-status and critical review. *J Environ Monit* 2008;10:1265–77.
- EA (Environment Agency). UKSHS report no. 1. Introduction and summaryUK soil and herbage pollutant survey; 2007.
- Fabietti G, Biasioli M, Barberis R, Ajmone-Marsan F. Soil contamination by organic and inorganic pollutants at the regional scale: the case of Piedmont, Italy. *J Soils Sediments* 2010;10:290–300.
- Heywood E, Wright J, Wienburg CL, Black HJ, Long SM, Osborn D, et al. Factors influencing the national distribution of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in British soils. *Environ Sci Technol* 2006;40:7629–35.
- Jiang Y-F, Wang X-T, Wang F, Jia Y, Wu M-H, Sheng G-Y, et al. Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China. *Chemosphere* 2009;75:1112–8.
- Jiang Y, Wang X, Zhu K, Wu M, Sheng G, Fu J. Polychlorinated biphenyls contamination in urban soil of Shanghai: level, compositional profiles and source identification. *Chemosphere* 2011;83:767–73.
- Katsoyiannis A, Sweetman AJ, Jones KC. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. *Environ Sci Technol* 2011;45:8897–906.
- Liu S, Xia X, Yang L, Shen M, Liu R. Polycyclic aromatic hydrocarbons in urban soils of different land uses in Beijing, China: distribution, sources and their correlation with the city's urbanization history. *J Hazard Mater* 2010a;177:1085–92.
- Liu Y, Chen L, Zhao JF, Wei YP, Pan ZY, Meng XZ, et al. Polycyclic aromatic hydrocarbons in the surface soil of Shanghai, China: concentrations, distribution and sources. *Org Geochem* 2010b;41:355–62.
- Ma W-L, Li Y-F, Sun D-Z, Qi H. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in topsoils of Harbin, China. *Arch Environ Contam Toxicol* 2009;57:670–8.
- Maliszewska-Kordybach B, Smreczak B, Klimkowicz-Pawlas A. Effects of anthropopressure and soil properties on the accumulation of polycyclic aromatic hydrocarbons in the upper layer of soils in selected regions of Poland. *Appl Geochem* 2009;24:1918–26.
- Morillo E, Romero AS, Maqueda C, Madrid L, Ajmone-Marsan F, Grcman H, et al. Soil pollution by PAHs in urban soils: a comparison of three European cities. *J Environ Monit* 2007;9:1001–8.
- Motelay-Massei A, Ollivon D, Garban B, Teil MJ, Blanchard M, Chevreuil M. Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere* 2004;55:555–65.
- Nadal M, Schuhmacher M, Domingo JL. Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environ Pollut* 2004;132:1–11.
- Nadal M, Schuhmacher M, Domingo JL. Levels of metals, PCBs, PCNs and PAHs in soils of a highly industrialized chemical/petrochemical area: temporal trend. *Chemosphere* 2007;66:267–76.
- Nadal M, Schuhmacher M, Domingo JL. Long-term environmental monitoring of persistent organic pollutants and metals in a chemical/petrochemical area: human health risks. *Environ Pollut* 2011;159:1769–77.
- Nam JJ, Sweetman AJ, Jones KC. Polynuclear aromatic hydrocarbons (PAHs) in global background soils. *J Environ Monit* 2009;11:45–8.
- Oliveira C, Martins N, Tavares J, Pio C, Cerqueira M, Matos M, et al. Size distribution of polycyclic aromatic hydrocarbons in a roadway tunnel in Lisbon, Portugal. *Chemosphere* 2011;83:1588–96.
- Peng C, Chen W, Liao X, Wang M, Ouyang Z, Jiao W, et al. Polycyclic aromatic hydrocarbons in urban soils of Beijing: status, sources, distribution and potential risk. *Environ Pollut* 2011;159:802–8.
- Ravindra K, Sokhi R, Van Grieken R. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos Environ* 2008;42:2895–921.
- Srogi K. Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. *Environ Chem Lett* 2007;5:169–95.
- Tsai P-J, Shih T-S, Chen H-L, Lee W-J, Lai C-H, Liou S-H. Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station workers. *Atmos Environ* 2004;38:333–43.
- USEPA (U.S. Environmental Protection Agency). Volume I — human health evaluation manual (part B, development of risk-based preliminary remediation goals) EPA/540/R-92/2003. Risk assessment guidance for superfund. Washington DC: Office of Research and Development; 1991.
- USEPA (United States Environmental Protection Agency). Method 3540C — Soxhlet extraction. Revision 3. SW 846 test methods for evaluating solid wastes; 1996. <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3540c.pdf>.
- USEPA (U.S. Environmental Protection Agency). Regional screening levels for chemical contaminants at superfund sites. Regional screening table. User's guide; 2011. http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/usersguide.htm (Access date: July 2011).
- VROM (Ministry of Housing Spatial Planning and Environment Directorates). Circular on target values and intervention values for soil remediation: BO/1999226863. General for environment protectionDepartment Of Soil Protection, Netherlands Government Gazette, No. 39; 2000. http://www2.minvrom.nl/Docs/internationaal/annexS_I2000.pdf.
- Wilcke W. Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. *Geoderma* 2007;141:157–66.
- Wu S, Xia X, Yang L, Liu H. Distribution, source and risk assessment of polychlorinated biphenyls (PCBs) in urban soils of Beijing, China. *Chemosphere* 2011;82:732–8.
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 2002;33:489–515.
- Zhang HB, Luo YM, Wong MH, Zhao QG, Zhang GL. Concentrations and possible sources of polychlorinated biphenyls in the soils of Hong Kong. *Geoderma* 2007;138:244–51.
- Zhang XL, Tao S, Liu WX, Yang Y, Zuo Q, Liu SZ. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. *Environ Sci Technol* 2005;39:9109–14.