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ORIGINAL PAPER

Urban geochemistry and potential human health risks in the Metropolitan Area of Buenos Aires: PAHs and PCBs in soil, street dust, and bulk deposition

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Abstract Soil, street dust, and bulk deposition (dry and wet deposition) were collected in the Metropolitan Area of Buenos Aires (MABA), Argentina, to assess the polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) pollution and the potential risks to human health. Compared with other countries, the mean concentration of PAHs and PCBs in surface soils, street dust and bulk deposition of MABA were at a low or moderate level. Average PAHs and PCBs concentrations in bulk deposition (5.7 ± 5.1 and 0.41 ± 0.25 μg g^{-1}, respectively) were five and ten times higher than those of soil (1.08 ± 0.98 and 0.02 ± 0.01 μg g^{-1}) and street dust (1.2 ± 0.95 and 0.04 ± 0.03 μg g^{-1}), respectively. Different compositional profiles, observed in the three matrices for both groups of contaminants, could be attributed to dissimilar source contribution, partition processes between gas and particulate phases, and transformation. The most contaminated bulk deposition presented higher values for cancer and non-cancer risks relative to soil and street dust. In all matrices, non-carcinogenic risks were below the safety threshold (HI < 1). Regarding carcinogenic risks, exposure to both bulk deposition and soil indicated a moderated potential for cancerous development (Incremental lifetime cancer risk $\sim 3.0 \times 10^{-6}$).

Keywords PAHs · PCBs · Soil · Street dust · Bulk deposition · Human health risk

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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 urban environment (Calesso Teixeira et al. 2015; Glüge et al. 2016). PAHs have been extensively studied because of their potential mutagenic and carcinogenic effects (IARC

2010). PCBs have been linked to a wide range of human health and ecosystem effects, in particular neurodevelopmental, reproductive, and endocrine-related effects, even at relatively low PCB doses (ATSDR 2000). Therefore, both groups of pollutants may exert potential health risk to urban residents. PAHs are released into the urban environment mainly through anthropogenic activities such as vehicle emissions, coal and fossil fuel combustion for power generation, firewood burning, oil spills and coal tars (Larsen and Baker 2003; Wang et al. 2013). On the other hand, PCBs were intentionally synthesized and used as heat transfer fluids, hydraulic lubricants, and dielectric fluids. Although the production and usage of PCBs were prohibited through the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2004 worldwide, they are still present in materials with a long-use phase as sealants of concrete buildings and paints (Jartun et al. 2009; Robson et al. 2010), and they can also be formed as by-products of certain industrial processes or waste incineration (Yu et al. 2006; Nakao et al. 2006). Thus, substantial amounts of PCBs are still emitted from primary and secondary sources in cities (Diamond et al. 2010; Diefenbacher et al. 2016).

PAHs and PCBs 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 and surfaces after dry and wet atmospheric deposition (Montelay-Massei et al. 2004). Hence, atmospheric deposition is considered as an important removal pathway of hazardous pollutants from the atmosphere into the aquatic and terrestrial ecosystem (Franz et al. 1998; Tasdemir et al. 2004). Accordingly, urban surface dust represents a hazardous carrier of organic compounds which exerts a dynamic relationship with atmospheric aerosol by resuspension into and redeposition from the atmosphere and should be considered as an air pollutant of concern (Han et al. 2009). Indeed, street dust may be a good indicator of toxic pollutants deposited from the atmosphere (Wang et al. 2011a; Tang et al. 2013), and several studies have shown its potential health and environmental impact (Ferreira-Baptista and De Miguel 2005; Soltani et al. 2015). On the other hand, many studies on bulk (wet and dry) deposition of PCBs and PAHs have been used to estimate the influence of atmospheric inputs of organic pollutants on the surface environment (Demircioglu et al. 2011; Cavalcante et al. 2012). These studies provide information on the contaminant fluxes, allow doing a comparison of contamination in different areas, and can also yield information about the sources affecting the area. However, there are no studies which have applied a health risk assessment model to bulk deposition. The risk assessment strategies have been widely used to evaluate the potential risks that soil pollutants pose to human health and currently it has been extended to the risk evaluation of street, indoor and outdoor dust exposure (Ferreira-Baptista and De Miguel 2005; Wang et al. 2011b; Cachada et al. 2012; Jiang et al. 2014).

The Metropolitan Area of Buenos Aires (MABA) is considered one of the ten greatest urban conglomerates in the world and the third mega-city in Latin America, following Mexico City (Mexico) and Sao Paulo (Brazil). It is comprised by the city of Buenos Aires and the Gran Buenos Aires with a total area of 4000 km^2 and about 13 million inhabitants. The MABA is a highly industrialized area (petrochemical, chemical, textile, shipyard, and metal processing industries), where most of the industries are located in districts near Buenos Aires Port and Matanza-Riachuelo basin. The purposes of this research were to (1) assess the PAH and PCB concentrations in soil, street dust, and bulk deposition in MABA (2) contrast pollutant compositions in the three matrices and (3) examine the human health risks for exposure to soil, street dust and bulk atmospheric deposition, via inhalation, ingestion and dermal contact of both children and adult.

Materials and methods

Study area and sampling

This study was conducted at Avellaneda, Lanus, and Berazategui counties, located at the MABA in the Buenos Aires city southeast (Fig. 1). This area is the most urbanized region of the state, and it is characterized by various types of industries (e.g., oil refineries, chemicals, tannery, steel, and fuel oil—natural gas power plants). Sampling locations in selected counties reported above were chosen because of their vehicular and industrial influences. Sites 1 and 6 have direct vehicular influence characterized by light- and heavy-duty fleet, traffic congestion, and

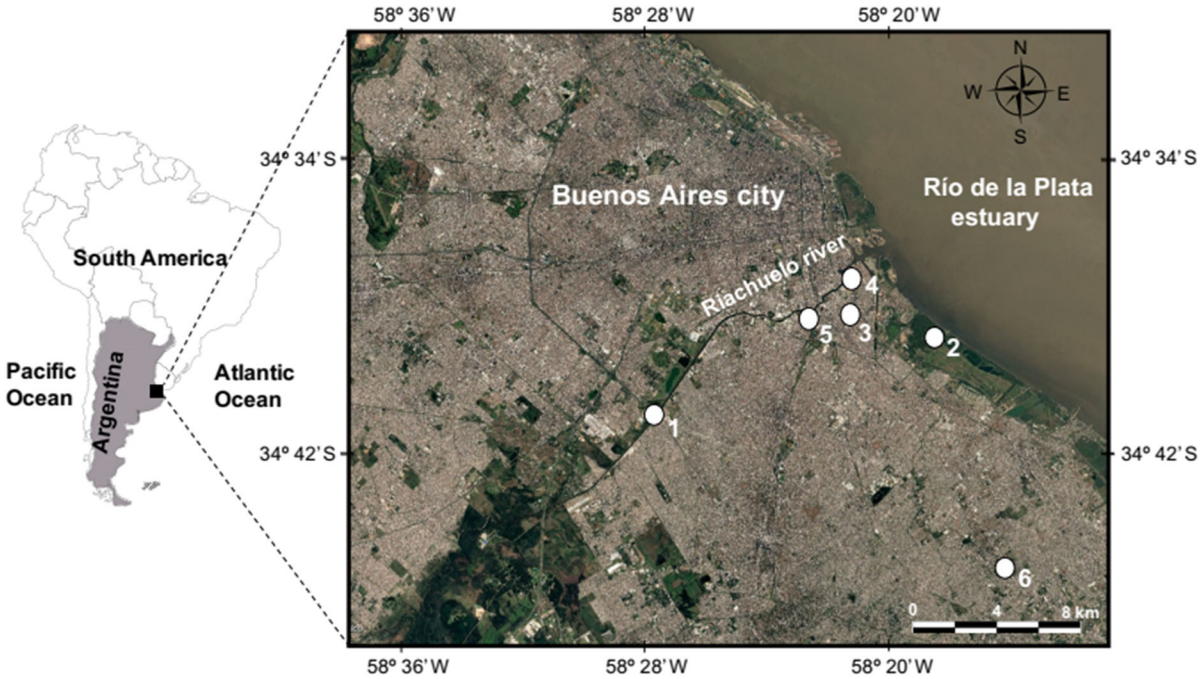

Fig. 1 Sampling sites at the Metropolitan Area of Buenos Aires (MABA; Image: Google, DigitalGlobe)

there are almost no nearby industrial plants. Sites 3, 4, and 5 have vehicular influence, light duty, slow vehicle speed, and they are placed at 2 km (sites 3 and 4), and 4 km (site 5) from a large industrial complex of power plants, oil refineries, and coking plant. Site 2 is located in an urban nature reserve without vehicular influence at 2 km from the industrial complex in front of an old municipal waste dumping site.

In every site, dry and wet depositions (bulk deposition) were obtained during two periods between August and October 2015, and 1–3 composite samples of at least 3 subsamples of topsoil (0–5 cm) were collected in a glass flask using a stainless steel shoves in August of 2015 (n = 10). In sites where there was deposit dust on a paved surface, 1–2 composite samples (three subsamples separated 1–2 m from each other) of street dust were also collected in a glass flask (n = 5; Table 1). Bulk deposition samples were collected during two monthly periods (n = 12) in glass jars (10 cm of inner diameter and 14 cm high). The jars were placed so that their top edges were 2 meters above the ground into a plastic cylinder to prevent bird fouling and light incidence over sample. Before sampling, about 1.0 l of purified water and copper sulfate were added to each sampler to reduce resuspension loss of deposited particles and to prevent algal growth. Following sampling, jars were sealed, brought to the laboratory and immediately filtrated through pre-combusted weighed 47 mm-diameter glass filters (Munktel MGF; 0.70 µm). The jars were subsequently rinsed with purified water. The filters were dried at 40 °C for 24 hs and weighed to determine dry mass and stored at − 18 °C until organic extraction.

Analytical method

Homogenized soil and street dust samples were separate for water content determination (24 hs; 100 °C), organic content (TOC; ignition loss; 12 hs, 450 °C), organic grain size analysis by sieve and pipet method; (Gee and Bauder 1986), and organic trace compound determinations (about 10 g of wet material).

For determination of trace organics, subsamples of soil and street dust, filters, and blanks were spiked with internal standards (PCBs 103 and 198; Absolute Standard; deuterated phenanthrene-d10 and chrysene-d12 Accustandar Inc.), and they were extracted with acetone/dichloromethane/petroleum ether (1:2:2) in an ultrasound bath. The extracts were concentrated

Table 1 Sampling sites, ignition loss, and grain size composition of soil and street dust samples

Site	Coordinates	Characteristic	Potential pollution source	Sample	Ignition loss (%)	Sand (%)	Silt (%)	Clay (%)
1.	34°46′27.9″S 58°16′01.7″O	Front yard/ bus stop	High vehicular traffic, heavy-duty vehicles	Soil	5.61	52.0	34.6	13.4
				Street dust	1.44	83.3	14.4	2.3
2.	34°40′11.7″S 58°27′28.7″O	Farm land	Very low traffic, near dump	Soil	4.31	82.1	10.6	7.3
				Soil	11.0	16.3	55.5	28.1
3.	34°39′07.6″S 58°21′05.7″O	Park	Low traffic, industrial, and port areas	Soil	8.24	26.4	45.8	27.8
4.	34°38′29.4″S 58°21′18.4″O	Back garden	Domestic waste, low traffic, industrial, and port areas	Soil	6.84	49.3	34.3	16.4
				Soil	8.60	35.4	43.2	21.3
				Soil	7.63	39.3	39.8	20.9
				Street dust	6.75	55.6	29.1	15.3
5.	34°39′37.4″S 58°22′35.3″O	Park	Low traffic, railway station	Soil	9.53	31.4	50.7	18.0
				Soil	7.84	42.0	39.6	19.4
				Street dust	3.82	82.7	12.6	4.7
6.	34°42′14.1″S 58°27′34.5″O	Front yard/ bus stop	High vehicular traffic, heavy-duty vehicles	Soil	8.76	36.8	41.6	21.6
				Street dust	1.55	88.5	9.0	2.5
				Street dust	3.39	77.5	16.3	6.2

under nitrogen and fractionated by silica gel column chromatography to obtain PCBs and PAHs fractions by successive elutions with petroleum ether and petroleum ether–dichloromethane (Colombo et al. 2005).

The PCBs in the first eluate were analyzed by an Agilent 7890 gas chromatograph equipped with a DB-5 capillary column (30 m 0.32 mm 0.25 mm) and an electron capture detector. Details of chromatograph conditions and temperature programs are given in Supplementary material. The external standard method was used to determine 41 congeners: tri-CBs: 17, 18, 31/28, 33/53; tetra-CBs: 44, 49, 52, 70, 74; penta-CBs: 87, 95, 99, 101, 110, 118; hexa-CBs: 128, 132/105, 138, 151/82, 153, 156,158, 169; hepta-CBs: 170, 171, 177, 180, 183, 187,191; octa-CBs: 194, 195, 199, 205; nona-CBs: 206, 208; deca-CBs: 209.

The PAHs in the final eluate were analyzed by an Agilent 7890 gas chromatograph equipped with an HP-5 capillary column (30 m 0.32 mm 0.25 mm) and a selective detector tandem MS/MS (Waters-Micromass Quattro Micro). Injector and oven conditions were the same that PCB analysis (see Supplementary material). Mass spectrometer conditions were as follows: ionization mode at EI (70 eV), interface temperature at 280 °C, ion source temperature at 180 °C, and quadrupole temperature at 150 °C. The detector was set to Selective Ion Monitoring mode. The external standard method was used to determine 17 USEPA priority PAHs, namely naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), chrysene (CHR), benz(a)anthracene (BaA), benzo(k)fluoranthene (BkF), benzo(b)fluoranthene

(BbF), benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), dibenz(a,h)anthracene (DBA), indeno(1,2,3-cd)pyrene (IND), and benzo(g,h,i)perylene (BghiP). Ions m/z 152, 162, 178, 188, 202, 228, 240, 252, 276, and 278 were monitored for PAHs calculation.

The detection limits (3:1 signal to noise) ranged from 0.2 to 20 ng g^{-1} dry weight for PAHs and 0.1 to 3.0 ng g^{-1} dry weight for PCBs. Procedural blanks (one for every batch of seven samples) were below the detection limits and surrogate recovery ranged between 43 ± 15 and 78 ± 27% for PAHs and PCBs, respectively. Recovery efficiencies were determined by analyzing the standard reference material (SRM), 1944 National Institute of Standards and Technology (NIST, USA). Recoveries of the certified reference materials were 74 ± 12% for PCBs and 74 ± 7.1% for PAHs (Table 1S and 2S).

Exposure and risk assessment

The model used in this study to calculate the exposure of children and adults to PCBs and PAHs in soil, street dust, and bulk deposition is based on those developed by US Environmental Agency (USEPA 1991a). Exposure is expressed in terms of daily dose, and it is calculated separately for each pollutant and exposure pathway (ingestion, inhalation, and dermal contact) as shown in Eqs. (1)–(3).

Dose contracted through ingestion:

$$D_{\mathrm{ing}} = \frac{C \times \mathrm{Ing}R \times F \times \mathrm{ED} \times 10^{-6}}{\mathrm{BW} \times \mathrm{AT}} \quad (1)$$

Dose contracted through inhalation of particles:

$$D_{\mathrm{inh}} = \frac{C \times \mathrm{Inh}R \times F \times \mathrm{ED}}{\mathrm{PEF} \times \mathrm{BW} \times \mathrm{AT}} \quad (2)$$

Dose contracted through dermal contact:

$$D_{\mathrm{derm}} = \frac{C \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{ABS} \times F \times \mathrm{ED} \times 10^{-6}}{\mathrm{BW} \times \mathrm{AT}} \quad (3)$$

where C is the concentration of pollutant in soil, street dust or bulk deposition, Ing$R$ and Inh$R$ are ingestion and inhalation rate, F is the exposure frequency; BW the body weight, ED the exposure duration; SA the exposed skin area; ABS the dermal absorption factor; AF the skin adherence factor; PEF the particle emission factor; and AT average time. All parameters used in the model for children (6 years old) and adults (30 years old) are based on the Risk Assessment Guidance of US EPA and related publications (Table 2).

The concentration term, C (mg kg^{-1}) is the upper limit of 95% confidence interval for the mean (USEPA 2002). The doses of each pollutant and exposure pathway are subsequently divided by the corresponding reference dose (RfD; Health Canada 2007; USEPA 2017) to yield a hazard quotient (HQ). An overall hazard index of soil (HI_{soil}), street dust (HI_{dust}), or bulk deposition (HI_{bulk}), were measured by summing up HQs for all pollutants and exposure pathways. An HI < 1 indicates that there is no significant risk of non-carcinogenic effects. Conversely, an HI > 1 indicates that there is a chance of non-carcinogenic effects occurring, with a probability that tends to increase as the value of HI increases (USEPA 1991a).

In order to estimate the carcinogenic potency, PAHs toxicities were calculated based on the set of benzo[a] pyrene toxicity equivalency factors (TEFs) of PAHs (USEPA 1993). The carcinogenic potency of total PAHs (BaPeq) is obtained by summing the toxic benzo[a] pyrene equivalent concentrations of each PAHs, as follows:

$$\mathrm{BaPeq} = \sum(\mathrm{PAH}_i \times \mathrm{TEF}_i)$$

where PAH_i is the concentration of the PAH congener i, TEF_i is the toxic equivalent factor for the PAH congener i and BaPeq is the toxic equivalent concentration of the sample. In this study, potential cancer risk as a result of being in contact with PAHs contaminated soil, street dust or bulk deposition was estimated by the incremental lifetime cancer risk (ILCR; USEPA 1991a) in terms of direct ingestion, dermal contact and inhalation are as follows:

$$\mathrm{ILCR} = (\mathrm{CSF}_{\mathrm{ing}} \times \mathrm{D}_{\mathrm{ing}}) + (\mathrm{CSF}_{\mathrm{derm}} \times \mathrm{D}_{\mathrm{derm}}) + (\mathrm{CSF}_{\mathrm{inh}} \times \mathrm{D}_{\mathrm{inh}})$$

ILCR reflects the likelihood that people got cancer on account of ingestion, inhalation, and dermal contact to the matrices contaminated by carcinogenic PAHs. The acceptable level is equal or lower than 10^{-6} (USEPA 1991b). D_{Ing}, D_{derm} and D_{Inh} are calculated as Eqs. (1)–(3); CSFs are carcinogenic slope factors (mg kg^{-1} $day^{-1})^{-1}$. $\mathrm{CSF}_{\mathrm{Ingestion}}$, $\mathrm{CSF}_{\mathrm{Dermal}}$ and

Table 2 Parameters used in the risk health assessment

Exposure variable	Units	Adult	Child	
Soil intake rate (ing*R*)	mg day^{-1}	100	200	USEPA (1991b)
Inhalation rate (inh*R*)	m^3 day^{-1}	16	10	USEPA (2011)
Exposure frequency (*F*)	days year^{-1}	180	180	Ferreira Baptista and De Miguel (2005)
Exposure duration (ED)	year	30	6	Ferreira Baptista and De Miguel (2005)
Body weight (BW)	kg	72	19	USEPA (2011)
Average life exposure non-cancer (AT)	days	10,950	2190	USEPA (1991b)
Average life exposure cancer (AT)	days	25,550	25,550	USEPA (1991b)
Dermal surface exposure (SA)	cm^2	6940	2520	USEPA (2011)
Dermal adsorption fraction (ABS)	Dimensionless	0.1	0.1	USEPA (2004)
Dermal adherence factor (AF)	mg cm^{-2}	0.08	0.1	USEPA (2011)
Particle emission factor (PEF)	m^3 kg^{-1}	1.32E+09	1.32E+09	USEPA (1996)

$CSF_{Inhalation}$ of BaP, are 7.3 (USEPA 2017), 25 (Knafla et al. 2006) and 3.9 (mg^{-1} kg^{-1} day)$^{-1}$ (OEHHA 2017), respectively.

Statistical analyses

Statistical analyses including ANOVA, Tukey test for comparison of multiple samples, Pearson correlations for evaluation of the relationship between pairs of variables and principal component analysis (PCA) were carried out using XLSTAT (Addinsoft Pearson Edition 2014.5.03). Data are expressed as mean ± SD in dry weight, and a significance level of $p < 0{\cdot}05$, except otherwise indicated.

Results and discussion

PAH concentrations and sources

PAH concentrations for all matrices in this study (Table S3, Supplementary material) were compared among them and with data from different regions of the world (Table 5S). Total PAH concentrations in bulk deposition (5704 ± 5137 ng g^{-1}) were five times higher than soil and street dust concentrations (1077 ± 985 and 1205 ± 952 ng g^{-1}, respectively; $p < 0.001$). Compared with other countries, the mean concentration of PAHs in surface soils, street dust, and bulk deposition of MABA were at a low or moderate level. For example, the average soil concentration in this study was similar to that reported to an industrial area of Tarragona County, Spain (Nadal et al. 2004) and more than one order of magnitude lower than soils from London, UK, a historically polluted city (Vane et al. 2014). While the average of total PAHs in street dust of MABA was similar to that from Isfahan metropolis, Iran (Soltani et al. 2015) and four times lower than an industrial site of China (Jiang et al. 2014). Whereas the average of total PAHs in bulk deposition was less a half of that from large industrial cities Tianjin and Beijing, China (Wu et al. 2005; Wang et al. 2011b).

Correlation coefficients were measured between total and individual PAH compounds and organic matter content of soil and street dust. The results of the correlation test (Table 6S) showed that total PAHs and individual PAHs were not significantly correlated with organic matter content ($p < 0.05$), except ANT, BbF, BaP, BeP, IND, and BghiP. A likely reason for lack of correlation between TOC and most of PAHs may be the continuous input of fresh PAH contamination (non-equilibrium state). Others factors, such as proximity to the source, land use, the influence of deposition, may exert a stronger influence than organic matter on PAHs (Nam et al. 2008). In this study, high molecular weight PAHs, such as BbF, BaP, BeP, IND, and BghiP, were significantly correlated with organic matter. Jones et al. (1989a) reported that correlation among high molecular weight PAHs and organic matter reflects the greater binding capacity to soil organic matter of the higher molecular weight compounds.

In this study, the PAH patterns were dominated by PHE, FLT, and PYR (Fig. 2). Generally, this pattern is assigned to pyrogenic origin as fuel combustion products (Stogiannidis and Laane 2015). To assess the PAHs profiles, principal component analysis (PCA) was performed with the relative abundance of 17 PAHs in each sample. Figure 3 shows the PCA score plot for the two first components. The first component (PC1) accounts for a 37% of the total variance and is defined by the contribution of 5–6-ringed (+PC1) and 2–3-ringed PAHs (−PC1), the latter are the most vulnerable to atmospheric migration. The second factor (PC2), with 25% of the variance, has a prevailing contribution of indicators of pyrolytic origin FLT, PYR, and PHE (−PC2), opposites to the other PAHs (+PC2). The distribution of the samples shows that bulk deposition and soil are in opposite sides of PC1, suggest a contrasting between light molecular weight (LMW) contribution in deposition (−PC1) versus heavy molecular weight (HMW) compounds contribution in soil (+PC1), meanwhile street dust are at intermediate position. These results are consistent with previous findings that reported long-term enrichment of HMW PAHs in soils (Jones et al. 1989b). According to PC2, street dust samples are located on the negative side, showing the contribution of pyrolytic PAHs. Most of the bulk deposition and soil samples are in opposite side to street dust (+PC2), reflecting mixed sources or altered profiles of PAHs. This suggests that PAH profiles in bulk deposition and soil may be linked to various kinds of mobile and fixed sources such as industrial plants and industrial waste incinerators. Furthermore, PAHs can suffer degradation in the atmosphere by photolysis as well as by biotic and abiotic degradation when they are present in soils (Nadal et al. 2004).

Additionally, compositional ratios were used as a diagnostic source of PAHs, including FLT/(FLT + PYR) and IND/(IND + BghiP), as shown in Fig. 4. These ratios have been reported as more conservative since other ratios involving PAHs easily photodegraded, such as ANT and BaA, may be strongly influenced by photoreactions (Tobiszewski and Namiesnik 2012). The isomer ratios of FLT/(FLT + PYR) show a petrogenic–pyrogenic boundary near 0.4, with a ratio > 0.4 for pyrogenic sources (Yunker et al. 2002). FLT/(FLT + PYR) ratios for street dust ranged from 0.34 to 0.40 (0.40 ± 0.06) in the present study, implying gasoline and diesel combustion, exhaust diesel—particle and vapor of unburned diesel-—and lubricating oil product as predominant PAHs sources (Larsen & Baker 2003). FLT/(FLT + PYR) ratios ranged from 0.48 to 0.54 (0.51 ± 0.02) in the soil, consistent with liquid fossil fuel (vehicle and crude oil) as combustion sources. FLT/(FLT + PYR) ratios ranged from 0.45 to 0.58 (0.53 ± 0.04) in bulk deposition, reflecting a clear pyrogenic influence with exception of site 2—reserve area—where the ratio was < 0.4. FLT/(FLT + PYR) ratios in site 2 might indicate that other diffuse sources have greater influence than traffic in this area.

Another widely used indicator is the IND/(IND + BghiP). A ratio lower than 0.2 implies petroleum products, between 0.20 and 0.50 a liquid fossil fuel combustion, and higher than 0.50 suggests a grass, wood or coal combustion (Yunker et al. 2002). In the present study, almost all samples were characterized by IND/(IND + BghiP) ratios ranged from 0.21 to

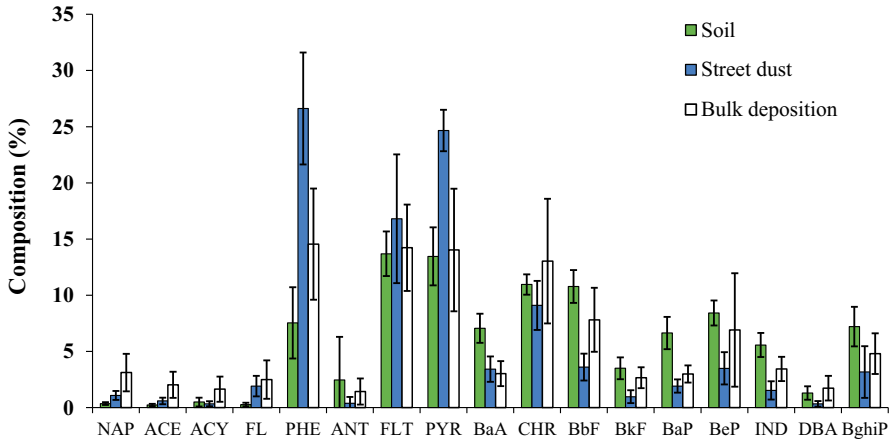

Fig. 2 PAHs composition in soil, street dust and bulk deposition (average ± SD)

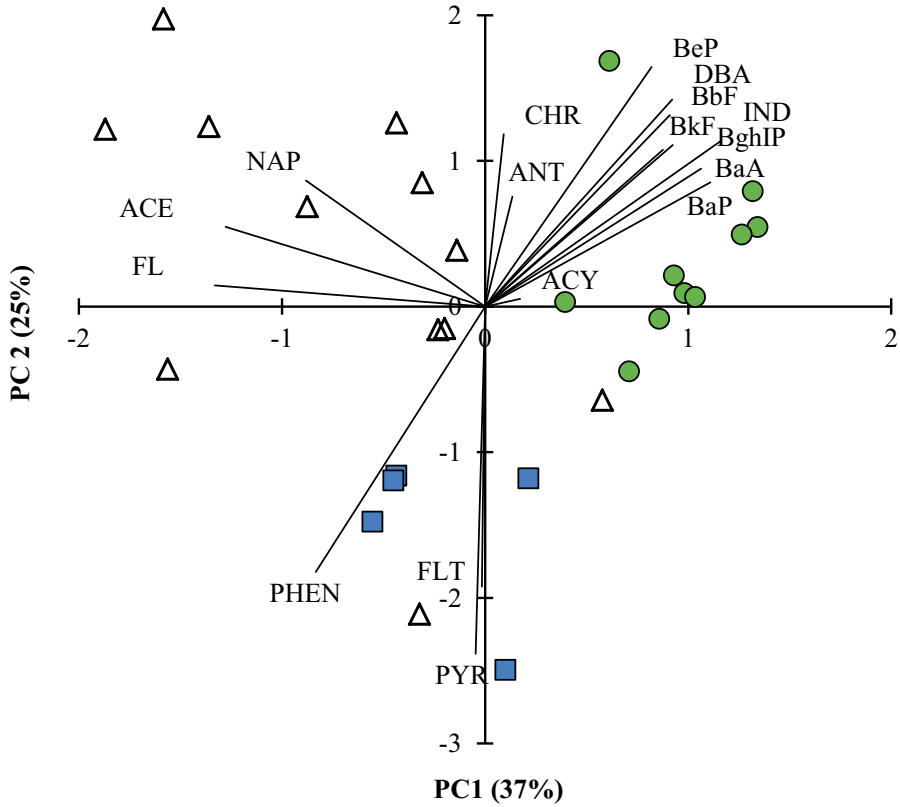

Fig. 3 Principal component analysis performed with relative abundance of individual PAHs in soil (circles), street dust (square) and bulk deposition (triangle)

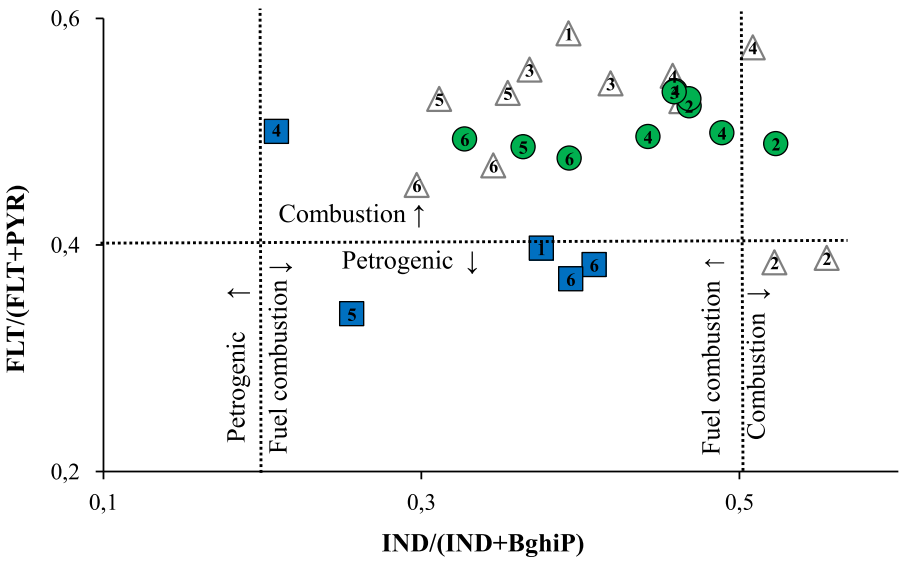

Fig. 4 Diagnostic PAH ratios calculated for soil (circles), street dust (square) and bulk deposition (triangle). The internal numbers indicate the sampling site

0.51 indicating a fuel combustion origin of PAHs, except bulk deposition in site 2 where pyrogenic wood and coal combustion were suggested as PAHs sources. Overall, both ratio results suggest that the most important PAHs sources were fossil fuel combustion from automobiles in soil and unburned petroleum residues in street dust. Others pyrogenic PAHs sources exhibited an influence in most deposition samples, differing in the sites without traffic impact where industrial complex may exhibit a major influence.

Although the PAH distribution patterns suggest a prevailing pyrogenic source in all matrices, PCA analysis showed that soil profiles were depleted in more volatile LMW compounds and isomers that may undergo faster desorption or more easily biodegradable such as PHE (Tobiszewski and Namiesnik 2012). As expected, street dust samples exhibited a plain profile influenced on combustion of gasoline and diesel due to road traffic exhaust emissions. Additionally, PCA suggested a higher contribution of LMW in bulk deposition. This latest result could be reflecting PAHs redistribution behavior from gas phases or fine aerosols to the coarse particle, which are main components of bulk deposition samples of this study (particles filter retained > 0.7 μm). In fact, PAHs are mainly emitted in the gas phase or associated with ultrafine particles and then become associated with coarse particles by volatilization and condensation (Offenberg and Baker 1999). According to Allen et al. (1996), the high molecular weight PAHs tend to remain on the fine particles with which they were emitted, while lower molecular weight PAHs tend to flow from the gas phase and the fine particles to the coarse particles by volatilization and condensation.

Concentrations and homolog patterns of PCB

The total and individual PCB concentrations for all matrices in this study are shown in Table 4S. PCB concentrations in bulk deposition (413 ± 252 ng g^{-1}) were about one magnitude order higher than those ones of soil (22 ± 9.8 ng g^{-1}), and street dust (41 ± 26 ng g^{-1}; $p < 0.001$). These values were comparable to other urban areas (Table S5). For example, average PCB concentrations in soil was three times higher than soils from urban sites of Portugal and Turkey (Cachada et al. 2012; Cetin et al. 2017), but lower than urban soils from London (Vane et al. 2014). On the other hand, PCB concentrations in street dust were one order of magnitude lower than street dust from urban sites of Germany (Klees et al. 2015) and polluted site of New York, USA (Irvine and Loganathan 1998). Regarding bulk deposition, Holsen et al. (1991) reported PCB concentrations in dry deposition from Chicago, USA, that were two orders of magnitude higher than those found in this study.

Correlation coefficients were measured among the total PCBs, homolog PCB groups and soil and street dust organic matter content. The correlation test results (Table 7S) showed that the total PCBs and homolog groups were not significantly correlated with the organic matter content ($p < 0.05$), except for the tetra-CBs (inversely correlated), and nona-CBs. These results are consistent with the PAHs trend, where a lack of correlation suggested non-equilibrium state, and a positive correlation of high weight compounds reflected their greater binding capacity to soil organic matter.

Figure 5 presents the averaged composition of PCBs in the three matrices discriminated by homolog groups. General composition in soil was dominated by hexa-, followed by penta- and hepta-CBs and minor contribution of tri-, tetra-, and octa- to deca-CBs. Street dust samples exhibited a comparable profile, dominated by hexa-, penta-, and hepta-CBs, but differed in the proportion of tetra-CBs. Even more different was the bulk deposition pattern dominated by hepta-, hexa-, penta-CBs followed by tri- and tetra-CB, with minor contribution octa- to deca-CBs. Soil and street dust profiles were dominated by penta- to hepta-CBs, as expected since the lower volatility of higher-chlorinated congeners imply they are bound to particles in heavily polluted areas (Meijer et al. 2002). Contribution of tri-CB, which have high atmospheric gas-phase concentrations (Astoviza et al. 2016), in the deposition samples may be due to (1) their association with large atmospheric particles, foliar debris, bacteria, or pollen that are collected by the deposition samplers, (2) their sorption to large surface dust aggregates that become suspended during high wind conditions, (3) particle scavenging, which is an extremely efficient mechanism of removal of PAHs and PCBs from the atmosphere (Offenberg and Baker 2002).

Additionally, PCB homolog distribution was tested by PCA according to the relative abundance of tri- to deca-CB (Fig. 6). The first (PC1) and second (PC2) components explained 45 and 28% of the variance, respectively. PC1 was determined by hexa-penta-CBs (+PC 1) and nona-deca-CBs (−PC 1), whereas PC2 was determinate by tri–tetra-CBs (+PC 2) and hexa-hepta-CBs (−PC 2). Most soil samples spread between penta, hexa and hepta-CBs in the right-lower side of the plot, in agreement with profiles reported of soils from Europe (Cabrerizo and Jones 2011). Street dust samples plot in the positive side of PC1, showing the contribution of tetra to hexa-CB, which seem to be the result of an overlay of industrial sources (Klees

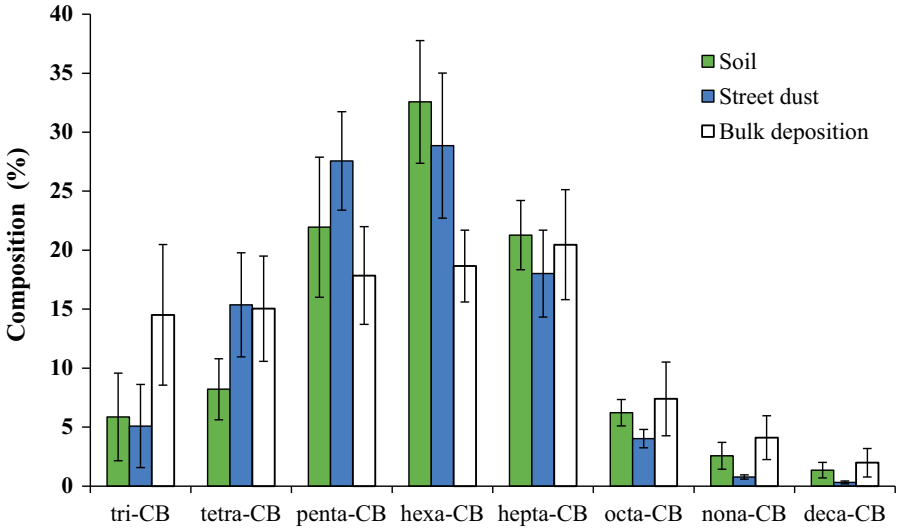

Fig. 5 PCB homolog composition in soil, street dust and bulk deposition (average ± SD)

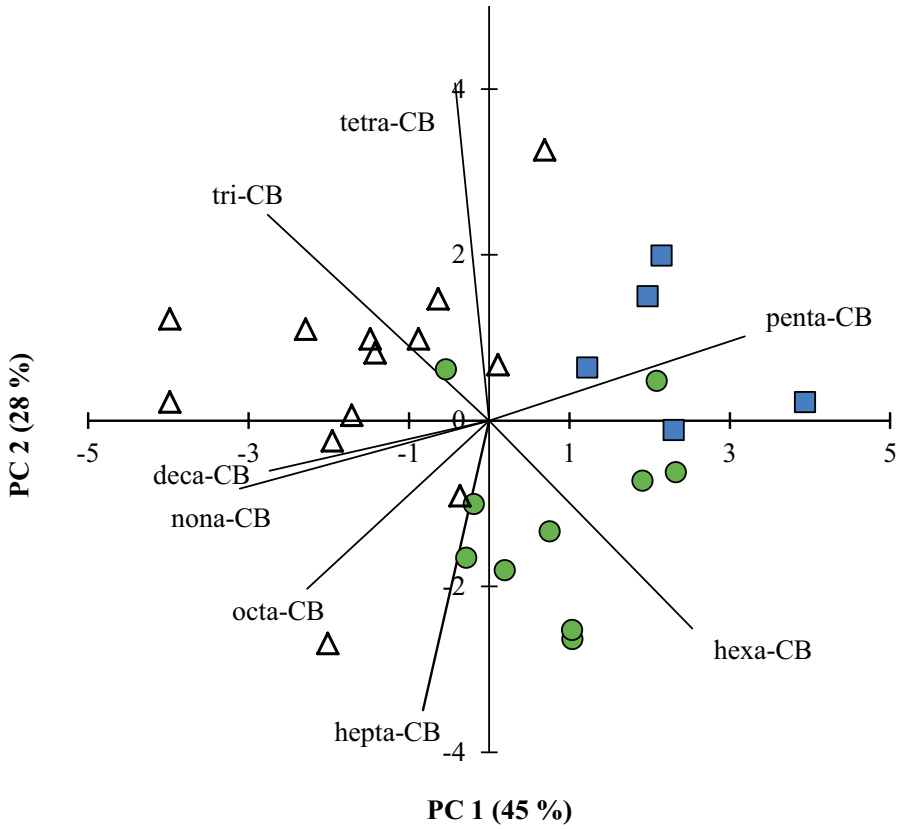

Fig. 6 Principal component analysis performed with relative abundance of individual PCBs in soil (circles), street dust (square), and bulk deposition (triangle)

et al. 2015). Bulk deposition samples are significantly shifted to −PC 1 and +PC 2, reflecting the contribution of high chlorinated PCB, as well as the contribution of tri–tetra-CB. These data are in agreement with processes of atmospheric distribution and

bound of lower chlorinated PCB to particle (Teil et al. 2004).

Risk assessment of PCBs and PAHs

Argentinian guidelines (Law 24.051, Decree: 831/93) establish target concentrations of nine individual PAHs (1–5 μg g^{-1}), and total PCBs (10 μg g^{-1}) for residential use of soil. In this study, measured PAH and PCB concentrations were lower than the values recommended by guidelines. They were also lower than the concentrations recommended by Canadian soil guidelines for the protection of environmental health at residential areas (CCME 2007, for PAHs (1–5 μg g^{-1}) and PCBs (1.3 μg g^{-1}).

Additionally, risk assessment results for soil, street dust, and bulk deposition exposure to PAHs and PCBs are shown in Tables 3 and 4. Besides, exposure doses and risk indexes for both children and adult in the study area are listed in Table 8S. Ingestion was the dominant exposure pathway to PCBs and PAHs for both subpopulations in the three matrices. Ingestion contributed 88.4% for to the total exposure doses in children, and the contribution of ingestion was 65.5% for total doses in adults. Dermal contact ranked the second contributor for the three routes, and accounted for 11.6 and 34.5% of the total exposure for children and adults, respectively. Therefore, inhalation contribution of dust particles for health risk is almost negligible when compared with the other exposure pathways in this study. A similar conclusion was also obtained in other reports (Ferreira-Baptista and De Miguel 2005; Soltani et al. 2015).

Children exposure to PAHs and PCBs was 1.5–6 times higher than the values for adults, which could be explained by children's hand to mouth and crawling behaviors (Roberts et al. 2009). In terms of main exposure pathway, ingestion doses order due to exposure to soil was: FLT > BaP > PCBs > ANTRA > NAP > FL > ACE, and they ranged from 4×10^{-8} to 3×10^{-6} mg kg^{-1} day^{-1}, and from 5×10^{-9} to 3×10^{-7} mg kg^{-1} day^{-1} for children and adults, respectively. The exposure doses resulted comparable to those ones reported for industrial and residential soils in Spain (Nadal et al. 2011). Regarding to street dust, the exposure doses order was FLT > PCBs > BaP > ANTRA > NAP > ACE > FL, and they ranged from 10^{-7} to 5×10^{-6} mg kg^{-1} day^{-1} and from 2×10^{-8} to 7×10^{-7} mg kg^{-1} day^{-1} for children and adults, respectively. For bulk deposition, the exposure doses resulted in the following order: FLT > PCBs > NAP > BaP > FL > ACE > ANTRA, and they ranged from 6×10^{-7} to 9×10^{-6} mg kg^{-1} day^{-1}, and from 8×10^{-8} to 10^{-6} mg kg^{-1} day^{-1} for children and adults, respectively.

Table 3 Exposure point concentration term (C, mg kg^{-1}), reference dose and total daily intake (RfD, TDI; mg kg^{-1} day^{-1}), hazard index (HI) for each compound and exposure route and for soil, dust, and bulk deposition

	PCB	BaP	NAP	ANTRA	ACE	FL	FLT	$HI_{soil/dust/bulk}$
RfD	0.00002	0.0003	0.02	0.3	0.06	0.04	0.04	
TDI ing	0.000007		0.02	0.3	0.06	0.04	0.04	
Soil								
C (95% UCL)	0.047	0.255	0.026	0.039	0.008	0.017	0.569	
HI = ΣHQ children	3.70E−02	5.10E−03	7.94E−06	7.74E−07	7.58E−07	2.55E−06	8.53E−05	0.042
HI = ΣHQ adults	5.44E−03	8.95E−04	1.39E−06	1.36E−07	1.33E−07	4.47E−07	1.50E−05	0.006
Street dust								
C (95% UCL)	0.090	0.077	0.050	0.051	0.028	0.024	0.970	
HI = ΣHQ children	7.11E−02	1.55E−03	1.51E−05	1.02E−06	2.75E−06	3.63E−06	1.45E−04	0.073
HI = ΣHQ adults	1.05E−02	2.71E−04	2.65E−06	1.78E−07	4.83E−07	6.36E−07	2.55E−05	0.011
Bulk deposition								
C (95% UCL)	0.624	0.299	0.378	0.111	0.143	0.177	1.772	
HI = ΣHQ children	4.94E−01	5.98E−03	1.13E−04	2.22E−06	1.43E−05	2.65E−05	2.66E−04	0.500
HI = ΣHQ adults	7.27E−02	1.05E−03	1.99E−05	3.89E−07	2.51E−06	4.66E−06	4.66E−05	0.074

Table 4 Risk of cancer due to human exposure to PAHs via soil, street dust, and bulk deposition

	Soil	Street dust	Bulk deposition
BaP eq (ng g^{-1}) 95% UCL	405	105	605
Children			
ILCRing	1.34E−06	3.48E−07	2.01E−06
ILCRInh	2.75E−11	7.12E−12	4.10E−11
ILCRderm	6.03E−07	1.56E−07	9.01E−07
ILCR	1.95E−06	5.05E−07	2.91E−06
Adults			
ILCRing	8.73E−07	2.26E−07	1.30E−06
ILCRInh	5.65E−11	1.47E−11	8.44E−11
ILCRderm	1.58E−06	4.09E−07	2.35E−06
ILCR	2.45E−06	6.35E−07	3.66E−06

Regarding to non-cancer risk, the HI values were lower than the safety threshold (HI < 1) in all matrices, with bulk deposition experiencing the highest level of non-cancer risks, followed by soil and street dust. HI values in soil were 0.042 for children and 0.0064 for adults, and PCBs and BaP had the greatest contribution to the index (about 87 and 13% of HI, respectively). HIs in street dust were 0.073 for children and 0.011 for adults, and PCBs and BaP contributed about 97 and 3% for the index, respectively. HIs in bulk deposition were 0.500 for children and 0.074 for adults, and PCBs and BaP also had the greatest contribution for the index, about 99 and 1%, respectively.

Results indicate that PCBs and BaP exhibited higher HQ values than the others compounds and the PCBs contribution to HI values increased in the following order: soil > street dust > bulk deposition. This latter fact would be related to the incorporation of pollutants (e.g., PCBs) from the atmosphere to the particles, which may cause a greater risk for exposure to the bulk deposition in comparison with the exposure to the soil or street material.

Regarding to PAH carcinogenic effects, the risk-based soil criterion for protection of human health from Canada indicates a safe level of 600 ng BaPeq g^{-1} (CCME 2007), and all soil samples showed concentrations lower than this guideline values (Table 3S). In addition, carcinogenic risk assessments due to exposure to BaPeq in soil, street dust, and bulk deposition are presented in Table 4. Dermal contact and ingestion pathways accounted for more than 99% of total risk. As already reported by other authors (Peng et al. 2011; Soltani et al. 2015), dermal contact had the highest contribution to adult risk (64% of total ILRC), whereas ingestion was the most dominant pathway for children risk (69% of total ILRC). Total ILRCs for exposure to soil via the three pathways were 1.9×10^{-6} and 2.4×10^{-6} for children and adults, respectively. In this study, ILRCs in soil were comparable to those ones reported for soils of urban areas of Portugal (Cachada et al. 2012). For street dust, ILRCs were 5.0×10^{-7} and 6.3×10^{-7} for children and adults, respectively, and they were one or two magnitude order lower than risk reported for the street dust of urban areas of China (Jiang et al. 2014), and Iran (Soltani et al. 2015). For bulk deposition, ILRCs values were 2.9×10^{-6} and 3.7×10^{-6} for children and adults, respectively. In this study, ILRCs values for bulk deposition were comparable to those ones reported for outdoor dust exposure in urban areas of China (Xu and Shu 2014; Kang et al. 2015). In addition, cancer risk of PAHs in bulk deposition was slightly higher than that of soil, and one magnitude order higher than that of street dust. Furthermore, cancer risk due to exposure via bulk deposition and soil exceeded 1.0×10^{-6} for both children and adults, indicating their potential carcinogenic risk.

Conclusion

The present study investigated the contamination of PAHs and PCBs in soil, street dust and bulk deposition in an urban area of Argentina; and their risks based on ingestion, inhalation, and dermal contact of residential children and adults. Overall, PAH and PCB concentrations were comparable with other cities, and the

results suggested that traffic and industrial contribute as PAH and PCB sources. Concentrations of PAHs and PCBs in bulk deposition were significantly higher than those concentrations in soil and street dust which may be related to the particle sources and/or the gas-particle partition of PAHs and PCBs in the atmosphere. Additionally, the deposition profile showed a higher contribution of the lighter compounds (LMW-PAHs and tri–tetra-CBs) in comparison with soil and street dust profiles. Our results might reflect the partition process of chemicals between gas-phase and atmospheric particles which determine removal of low molecular weight compounds from the atmosphere through wet and dry deposition. Exposure of bulk deposition exhibited the greatest risk to human health because of the higher PAH and PCB concentrations in the particles than those ones of soil or street dust, and different pollutant profiles. Therefore, our study support that measurements of chemical residues found in soil to determine the potential ingestion, inhalation, or skin absorption of a toxicant may result in an incomplete risk assessment.

Despite both of the limited number of samples and the uncertainty of the assumed parameter values in the USEPA models, which are not authentically applicable in the study area, this study provides an indication of the potential hazards. Regarding to the particle emission factor developed for soils, the application to less cohesive matrices (street dust and bulk deposition) has shown to negligible influence on the risk calculation since the hazard by inhalation is four to five magnitude orders lower than either dermal or ingestion exposure. Even with these limitations, the present study recognizes the relative risks among different pollutants, and it identifies the probable exposure pathway which results in the highest levels of risk for adults and children.

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