



Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in urban and semi-urban soils of Havana, Cuba

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Abstract

Purpose Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in Havana were quantified and analyzed in relation to possible emission sources to assess metropolitan soil contaminations in a highly dynamic, urban environment. The results of this study will serve Cuban legislators as a basis to develop environmental quality standards for organic pollutants in soils.

Materials and methods Possible emission sources as, e.g., the vicinity to roads or industrial plants and the influence of the land use were related to the organic contaminants concentrations. Therefore, 28 topsoils in the Havana urban and semi-urban area were sampled at agricultural ($n = 12$), organoponic (urban gardens in the capital, $n = 8$), public park ($n = 7$), and remediation (on-site bioremediation of an oil refinery, $n = 1$) sites. Their PAH and PCB concentrations were measured with gas chromatography mass spectroscopy and the total organic carbon (TOC) and black carbon (BC) concentrations with the chemo-thermal oxidation.

Results and discussion The sum of the 16 PAH concentrations ranged from 0.04 mg/kg in agricultural and organoponic soils to up to 72 mg/kg in a public park at about 1.5 km distance from an oil refinery. The lowest sum of the seven PCB congener concentrations was also measured in organoponic soils (0.002 mg/kg) and the highest in an arable patch of land between the rail roads and a main road (0.1 mg/kg). Both, PAH as well as PCB soil concentrations in Havana were almost up to two orders of magnitudes higher compared to a soil monitoring in the neighboring province of Mayabeque, but overall in the typical range of urban soils reported by other studies. The pollutants showed no relationship between TOC and BC except for PAHs with BC. For PAHs, combustion was the main source.

Conclusions A comparison of the pollutant concentrations with regulatory guidance values (RGV) of other countries revealed PCB concentrations in Havana soils far below these RGV. In contrast, some concentrations of benzo[*a*]pyrene, the most

carcinogenic PAH, in agricultural and park soils in Havana exceeded some RGV. Thus, some public parks pose a risk according to the Canadian quality guidelines when people have direct contact with these soils but not if they were consuming products thereof.

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1 Introduction

The World Bank indicated an increase in the Cuban gross domestic product (GDP) from 30.4 to 87.1 (current) billion US\$ from 1995 to 2015 (Valev et al. 2018). Tourism contributed substantially to this increase as in 2016 almost four million

tourists visited the island, whereas in 1995, there were only 742,000 (The World Bank 2018). The share of services as percent of GDP, where tourism is included, in the same time increased from 68 to 74% (Valev et al. 2018). The 2015 value is the same share as for the US and the UK (Valev et al. 2018). Many studies linked the GDP with urbanization and/or industrialization that was assessed by environmental pollutants (such as polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs) (Hong et al. 2012)), or with environmental quality indicators, such as carbon dioxide (Pata 2018) or with cancer incidence (Luzzati et al. 2018). To investigate this relationship, the present study assessed environmental impacts by means of persistent organic pollutants (POPs), such as PAHs and PCBs in the soils of the Havana metropolitan area (Havana became city and province in 2011 (Blanco and Moudon 2017). Here and throughout the article, “Havana” refers to the whole metropolitan area). This choice of Havana area-POPs-soil as investigated interactive matrix has several advantages over other environmental impact combinations. Firstly, most of the tourists that visited Cuban cities (40% in 2016 (ONEI 2017)) stayed in Havana (24% of tourists out of 100% (ONE 2011)). Secondly, PAHs and PCBs are perfect indicators for enhanced human activity in urban areas. PAHs are markers for the consumption of carbon energy and are formed by incomplete combustion (Dat and Chang 2017) of petroleum, diesel, fuel, ethanol, coal, wood, etc. PCBs were used in anti-corrosive paints, joint sealants, and electrical capacitors and transformers (Glüge et al. 2017), which was important in the construction of residential and industrial buildings. Indeed, a PCB inventory in Cuba, where whole industrial plants were imported from the former Soviet Union, revealed that the commercial transformer oil Sovtol was found in over 60% of all applications (Abo Balanza 2005). Both contaminant groups are ubiquitous and more than half of the PAHs investigated in this study are assigned persistent, bioaccumulative, and toxic (ECHA Version 5—24/03/2017). The PCBs (CAS 1336-36-3) belong to the 12 initially targeted POPs under the Stockholm Convention (Stockholm Convention 2008a). These chemicals do not only affect the human but also the environmental health (Dat and Chang 2017; Stockholm Convention 2008a). And thirdly, although both contaminant classes are mainly emitted into the air (Dat and Chang 2017; Glüge et al. 2017), Havana soil was monitored because the substances have a high affinity to partition into particles (Dat and Chang 2017) that later deposit, amongst others, onto soils (Cetin et al. 2017; Dumanoglu et al. 2017). Soils are the primary sink of POPs in the terrestrial environment because the contaminants strongly sorb to the soil organic carbon. The pollutants remain in the upper 10–20 cm of the matrix where organic carbon in form of humus is most present. The very high organic carbon to water partition coefficients (for PAHs, $\log_{10}K_{OC}$ values ranged from 2.3 for naphthalene to 7.0 for dibenz[*a,h*]anthracene and for PCBs from 5.3 for #28 to 5.9 for #153) demonstrates the affinity of PAHs and PCBs to the soil’s organic carbon (Bartolomé et al.

2018; Panagopoulos et al. 2017). The even stronger sorption of PAHs and PCBs to black carbon (BC), which forms part of the total organic carbon (TOC) in soils or sediments, pulls them into these matrices (Koelmans et al. 2006). Once bound to BC/TOC, the risk posed by the contaminants is reduced due to immobilization (Koelmans et al. 2006).

Although the source, as, e.g., PAHs co-emitted in soot from Diesel exhaust, may be more important in terms of bioavailability than the recipient matrix’ organic carbon concentration (Kołtowski et al. 2016; Bartolomé et al. 2018) soil, it qualifies as a good archive for these substances. The PAHs and PCBs persistency renders them as stock pollutants. With ongoing release, environmental concentrations are likely to increase over time (Gabbert and Hilber 2016). Stock pollutants accumulate in matrices like soil. Therefore, they create an intertemporal pollution problem, the impacts of which differ fundamentally from those of non-persistent chemicals (Gabbert and Hilber 2016).

The contribution of this study is therefore the systematic analysis of the environmental pollution in Havana metropolitan soils. This first data set shall serve, together with a similar study in rural soils of the Mayabeque province in Cuba (Sosa et al. 2017), as a basis for Cuban legislators to establish regulatory guidance values (RGV) that are up to now absent in the case of PAHs. However, Cuba nationally regulated total hydrocarbons of petroleum in tanks (Norma_Cubana_THC 2010) and PCBs, amongst others, in the environment (Norma_Cubana_PCB 2009) and signed (2001), ratified (2007), and entered into force (2008) the National Implementation Plan (Stockholm Convention 2008b) for the latter contaminants. Thus, this study will update the contamination status of PCB contamination in soils of the adopted directives in Cuba. In the long run, a Cuban soil monitoring network shall be developed where soils all over the country are regularly monitored over time to recognize spatial and temporal changes. That will, together with the Cuban legislation, pave the way for the precautionary principle.

The objectives of this study were to (i) assess the PAH and PCB soil concentrations in relation to different land uses in general, and, more specifically, to those determined earlier in Mayabeque province, i.e., a neighboring, but contrasting rural environment (Sosa et al. 2017), (ii) allocate PAH and PCB concentrations to potential emission sources, and (iii) investigate the influence of TOC and BC concentrations on PAH and PCB concentrations in the soils.

2 Material and methods

2.1 Area under investigation

The study was carried out in Havana (Fig. 1, 23° 07' 00" N and 82° 23' 00" W). Havana is the biggest city in Cuba with

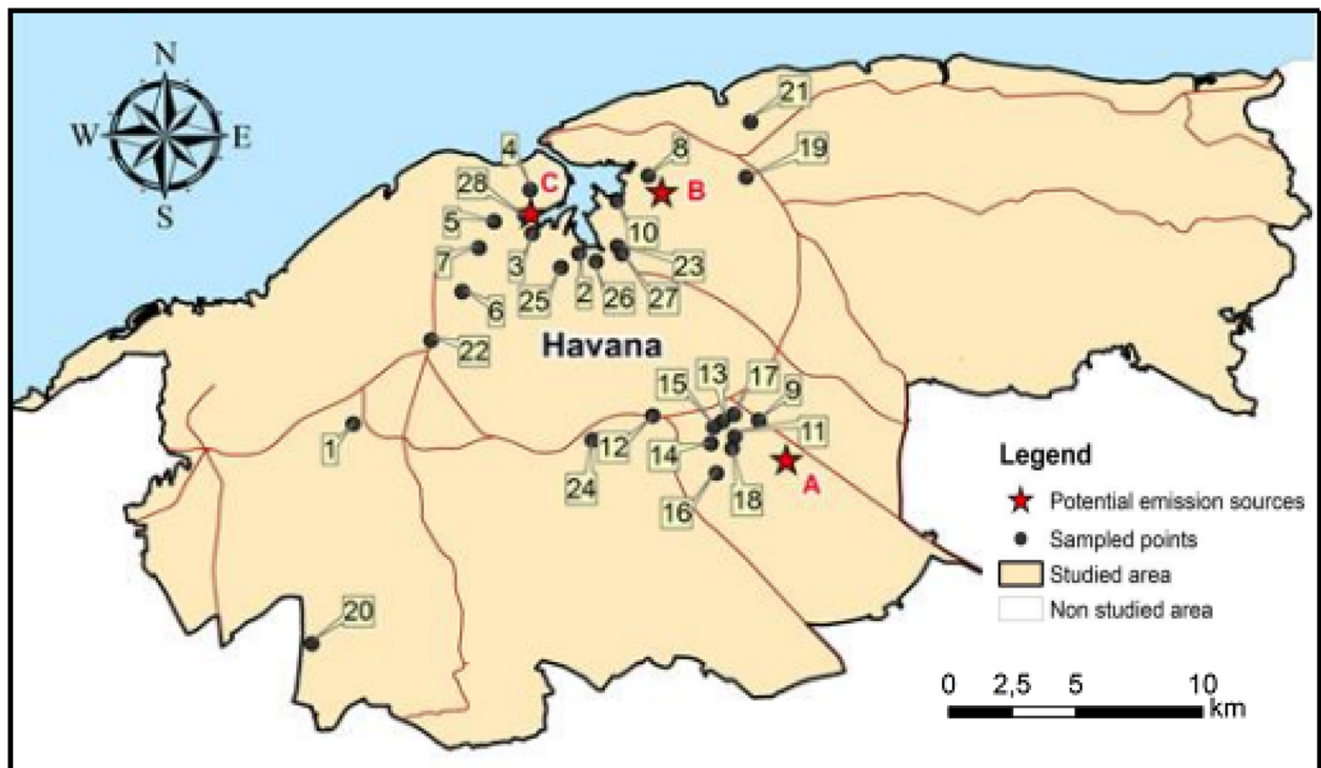


Fig. 1 Soil sampling sites (black dots numbered 1–28) in the province of Havana (for details, see Table S2, Electronic Supplementary Material). Presumed major point emission sources are marked with a red star. Red

capital letters specify source types: smelter power plant (A), refinery power plant (B), and thermoelectric industry (C)

2.1 million inhabitants (ONE 2010). They consumed most of the electricity (2.3 million Mw/h), fuel oil (56.600 t), gas oil (373.000 t), and gasoline (72.900 t) (ONEI 2016) in the period of 2011 to 2015 in comparison to all other provinces in Cuba. The area of Havana comprises 721 km², which is 0.7% of the surface of Cuba (ONEI 2016). Sixty-one percent of the province is dedicated to agriculture (crop 20%, livestock 21%, forestry 20% (ONEI 2016)).

Havana province has a humid tropical climate with an annual temperature between 21.8 and 30.4 °C and an average annual rainfall of 1129 mm (ONEI 2016). The rainy season (May to October) produces on average 170 mm rain per month and the dry season (November to April) 51 mm (data from the average monthly rainfall of the years 2010–2015) (ForesightCuba 2018). Although part of Havana province is sealed or consists of anthropogenic soils, the soil types of the Havana region are quite heterogeneous (Amaral Sobrinho et al. 2013; Medina et al. 2017). In the northeastern part, mainly cambisols (“pardos” according to the Cuban soil classification system) (AGRINFOR 1999) and fluvisols (“fluvisoles”) can be found classified in the system of the World Reference Base (IUSS Working Group WRB 2015). The cambisols are mainly associated to terrigenous carbonate rocks and the soils show a high calcium fraction in their base saturation. In contrast, ferrasols, nitisols, and lixisols (summarized as

“ferralíticos” in the Cuban soil classification system) predominate in the southern part. These soils are deeply weathered and typically show red or yellow colors and a high content of sesquioxides. Some smaller areas in the western part also reveal gleysols (“hidromórficos”), which have a gley horizon and marked hydromorphic properties. For further details with regard to soil types and soil properties, we refer to Amaral Sobrinho et al. (2013) and Medina et al. (2017).

2.2 Soil sampling and sample pretreatment

Soil samples ($n = 28$ for PAH analysis and $n = 27$ for PCB analysis without one remediation area) were collected between March 2015 and April 2016 at 28 different sites in Havana. The design of the survey is based on expert opinions of the Cuban research team, the Cuban Ministry of Science, Technology, and Environment of Havana city, and the Swiss Soil Monitoring Network (NABO) team that lead to a judgmental sampling pattern. The main criteria for the site selection were the principal pollution sources and the land uses (detailed information is provided in the Electronic Supplementary Material, Table S2).

The soil sampling followed the protocol of the NABO and is described in detail in Desaules et al. (2008) and Gubler et al. (2015). Briefly, in an area of 10 m by 10 m, four subsamples

were taken for each square meter with a steel gouge auger (3 cm inside diameter, 0–20 cm depth, including the humus layer) and bulked to four soil subsamples per site. The soil samples were dried at 40 °C, then crushed and sieved through a 2 mm mesh and stored in polyethylene bottles at 20–25 °C room temperature. Finally, an aliquot of 100 g was gathered per site of one subsample and shipped to Agroscope for analysis.

2.3 Analysis of PAHs and PCBs

The Cuban team analyzed the 16 PAHs (PAH16) prioritized by the US Environmental Protection Agency in the soil samples in the laboratory at Agroscope. The compounds were naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenz[*a,h*]anthracene (DBA), and benzo[*ghi*]perylene (BPE). The following seven PCBs (PCB7) were analyzed: #28, #52, #101, #118, #138, #153, and #180. The analysis of the PAH16 and the PCB7 in the soil samples is outlined in several references in detail (Bucheli et al. 2004; Brändli et al. 2005; Sosa et al. 2017). So, a Syncore Analyst (Büchi Labortechnik AG, Flawil, Switzerland) concentrated the samples that were extracted (10 g of soil, $n = 2$) before with a Soxhlet apparatus for 36 h with hexane to a volume of 1–2 mL. A separate cleanup for the PAHs than for the PCBs was performed by splitting the concentrated extract in two portions. One third of the extract was cleaned by *N,N*-dimethylformamide—Milli-Q water (9:1, *v/v*) liquid–liquid partitioning and then eluted over a column with water-deactivated silica gel to obtain an unsoiled sample for PAH analysis. The other two thirds of the aliquot were run over sodium sulfate and deactivated (10% Milli-Q water), potassium hydroxide-impregnated, and sulfuric acid-impregnated silica gel for the PCB analysis. The final extracts were separated for the analytes by gas chromatography and detected by mass spectroscopy (GC-MS, Agilent Technologies Model 6890N-5973). Sixteen deuterated PAHs and seven $^{13}\text{C}_{12}$ -labeled PCBs were injected to the soil samples prior to the Soxhlet extraction and served as internal standards to quantify the target analytes. The isotope-labeled extraction standards were spiked at concentrations of 20 and 5 $\mu\text{g}/\text{kg}_{\text{soil}}$ for PAHs and PCBs, respectively. Indeno[1,2,3-*cd*]fluoranthene served as recovery standard for PAHs and 1,2,3,4-tetrachloronaphthalene for PCBs. Both recovery standards were added to the final extracts immediately before injection into GC-MS. The calibration concentrations for individual PAHs ranged from 10 to 2500 $\text{pg}/\mu\text{L}$ that covered soil contaminations of about 0.75 to 250 $\mu\text{g}/\text{kg}_{\text{soil}}$ and from 5 to 250 $\text{pg}/\mu\text{L}$ that covered PCBs soil contaminations of about

0.5 to 25 $\mu\text{g}/\text{kg}_{\text{soil}}$. Linear calibrations were given over these concentration ranges.

2.4 Quality control and assurance

Average recoveries of the 16 deuterated PAHs and the seven $^{13}\text{C}_{12}$ -labeled PCBs ranged from 27 to 63% and from 66 to 94%, respectively (Table S3, Electronic Supplementary Material). Low absolute recoveries of light PAHs in particular were reported earlier already (Bucheli et al. 2004). Such losses were effectively compensated by the use of deuterated analogues, as indicated by relative recoveries of added PAHs in a blank sample between 93 and 108%. Average blank concentrations of individual PAHs ranged from 0.01 to 0.67 $\mu\text{g}/\text{kg}$ for BaP and NAP, respectively, and the sum (Σ) of the PAH16 was 2.31 $\mu\text{g}/\text{kg}$ (Table S3, Electronic Supplementary Material), which was slightly lower than 3.37 $\mu\text{g}/\text{kg}$ reported by Desaulles et al. (2008). Blanks of PCBs ranged from 0.1 for #52, #101 to 0.3 $\mu\text{g}/\text{kg}$ for #138 and #153 (Table S3, Electronic Supplementary Material) and were slightly higher than in Desaulles et al. (2008) that ranged from 0.013 to 0.16 $\mu\text{g}/\text{kg}$. All PAH and most of the PCB concentrations were above the blank values and not blank corrected because there is not necessary a causal relationship between a blank concentration and any of the samples. Method detection (MDL) and quantification (MQL) limits were calculated by three or ten times the noise over the respective signal times the concentration of the corresponding extract. The PAH MDL minimum was 0.09 $\mu\text{g}/\text{kg}$ for ANA and BkF and the MQL maximum was 3.36 $\mu\text{g}/\text{kg}$ for PYR. The MDL minimum for the PCBs were 0.12 $\mu\text{g}/\text{kg}$ for the congeners 101 and 153, and the MQL maximum was 1.5 $\mu\text{g}/\text{kg}$ for the #52 (Table S3, Electronic Supplementary Material). While almost all of the PAH concentrations were above the MQL (Table S4, Electronic Supplementary Material), most of the PCB #28, #52 concentrations were between MDL and MQL (Table S5, Electronic Supplementary Material). Although these values are not fully reliable but also not “not detected,” the concentrations were left as they were, because their fractions only contribute little to the ΣPCB7 in most samples. As a third quality control, the reproducibility as a measure of the method precision was assessed by repeated analysis of the well-characterized control soil sample of the NABO (KB6). The corresponding coefficients of variation (CV, standard deviation of replicates over mean in percent) ranged from 12 to 32% ($n = 7$) for PAHs and from 5 to 41% ($n = 2$) for PCBs (Table S3, Electronic Supplementary Material) and is acceptable for concentrations in the $\mu\text{g}/\text{kg}$ and mg/kg range (Horwitz 1982). An intra-laboratory comparison of the Cuban and the Swiss team did not reveal any statistical differences in the analytical results (p value > 0.99 , Table S3, Electronic Supplementary Material) where the Swiss team provides its analytical services for years to the NABO team.

An external quality control of the Agroscope laboratory is the successful participation in the Internal Sediment Exchange for Tests on Organic Contaminants (SETOC) of the Wageningen Evaluating Programs for Analytical Laboratories (WEPAL). Agroscope's average Zu-scores for 10 years of SETOC participation for instance for the 16 individual PAHs in 16 different samples per year is 0.19 with a standard deviation of ± 0.94 , which indicates good accordance with the rest of the 30 laboratories in Europe. Zu-scores are a relative scale consisting of the difference in reproducibility standard deviation between the consensus values and the laboratory results (Bachmann et al. 2016). For comparison, Zu-scores $> |3|$ are considered as outliers and ≤ 2 lie within the majority of the results and are considered inconspicuous (Bachmann et al. 2016).

2.5 BC and TOC analysis

BC and TOC analysis were described elsewhere (Agarwal and Bucheli 2011). For the BC analysis, the chemo-thermal oxidation method was used which consists of three parts: (1) removal of non-pyrogenic organic carbon from the dried (60 °C) and ball ground sample (15–20 mg) in a programmable tube furnace (LOBA 1200-80.600-1-OW with quartz tube 75/70 mm \times 10,000 mm from HTM Reetz GmbH, Berlin, Germany) at 375 °C under controlled air flow, (2) removal of inorganic carbonates via acid fumigation for 4 h in a desiccator with 12 M hydrochloric acid, and (3) quantification of residual carbon as BC using a CHN elemental analyzer (Euro EA 3000 Elemental Analyzer, Eurovector SPA, Milan, Italy). TOC was determined in a similar way but without stage 1 of the BC method. All data were determined in triplicates. The BC MDL was 0.23 g/kg (Agarwal and Bucheli 2011).

2.6 Data presentation and analysis

Descriptive statistics for data presentation were carried out with Excel Office 2013, InfoStat version 2010, and R version 3.4.3 (2017-11-30). Two one-way analyses of variance (ANOVA) with the land use as independent and the PAHs and PCBs as dependent variable, respectively, linear regressions (lin. regr.) with the TOC, BC, PAH, and PCB data, and a principal component analysis (PCA) were carried out with R version 3.4.3 too to evaluate the spatial and compositional pattern of the individual congeners. The PCA reduces dimensions in a complex data set and facilitates the interpretation and is therefore a widely used technique (Jolliffe 2011). Dimensions are reduced by finding linear combinations of $a_1'x, a_2'x, \dots, a_q'x$, where x are vectors of p random variables running from p to q , called principal components, that have maximum variance for the data (Jolliffe 2011). Solving this maximization problem, the vectors a_1, a_2, \dots, a_q are the eigenvectors of the covariance matrix of the data corresponding

to the q largest eigenvalues (Jolliffe 2011). The biplot depicts the two principal components and the vectors in a chart. Statistically significant influence was denoted at a p value ≤ 0.05 . Prior to any statistical analysis, the concentrations were log transformed to achieve normal distribution and the ANOVA output was, due to unequal group sizes, checked for normal distribution of the residuals and homoscedacity of the variance of the residuals. For both, PAHs and PCBs ANOVA analysis, these prerequisites were fulfilled.

3 Results and discussion

3.1 PAH concentrations

Total concentrations of the sum Σ PAH16 of the 28 soil samples in Havana are depicted in Fig. 2a. Agricultural plots ($n = 12$, 0.04–2.7 mg/kg) and organoponic gardens ($n = 8$, 0.04–1.8 mg/kg) showed about the same Σ PAH16 concentration ranges although agricultural soils had the higher maximum value but a smaller interquartile range than organoponic gardens. City parks had the highest Σ PAH16 concentrations ($n = 7$, 0.4–72 mg/kg). The remediation area ($n = 1$, 43 mg/kg) belongs to a petroleum refinery in Havana. The company uses soil to clean their empty petroleum tanks, which is afterwards added to a field soil, homogenized, and disposed within the plant area on a field of 7.2 ha. The petroleum soil layer is weekly plowed to stimulate petroleum degrading microorganisms. In comparison to a recent soil monitoring of 39 soils in the Mayabeque province (Sosa et al. 2017), the majority of the Havana soils contained up to two orders of magnitude higher concentrations than its rural counterpart (max. concentration for Σ PAH16 was 0.1 mg/kg_{dry weight (dw)}).

Median (0.4 mg/kg) and maximum (16.9 mg/kg) PAH concentrations of agricultural soils from other studies (Wilcke et al. 1999b; Nam et al. 2003; Bucheli et al. 2004; Agarwal et al. 2009; Holoubek et al. 2009; Maliszewska-Kordybach et al. 2009; Lopez et al. 2011; Ortiz et al. 2012; Yang et al. 2012; Halfadji et al. 2017; Pokhrel et al. 2018) around the world were higher than soils from arable land and organoponics in this study (Fig. S1, Electronic Supplementary Material). In contrast, the minimum (0.01 mg/kg) was lower in agricultural soils from other studies around the world than in the Havana study (outlier Fig. S1B, Electronic Supplementary Material). PAHs in park soils from other parts of the world (Motelay-Massei et al. 2004; Biasioli and Ajmone-Marsan 2007; Wong et al. 2009; Vane et al. 2014; Jiao et al. 2017; Ke et al. 2017) showed the same range of contamination as Havana's parks. This also holds for PAHs from industrial sites in other studies (Fig. S1B, Electronic Supplementary Material (Nadal et al. 2004; Zhang et al. 2006; Nadal et al. 2011; Nieuwoudt et al. 2011; Khillare et al. 2014; Teng et al. 2015; Pokhrel et al. 2018)) when

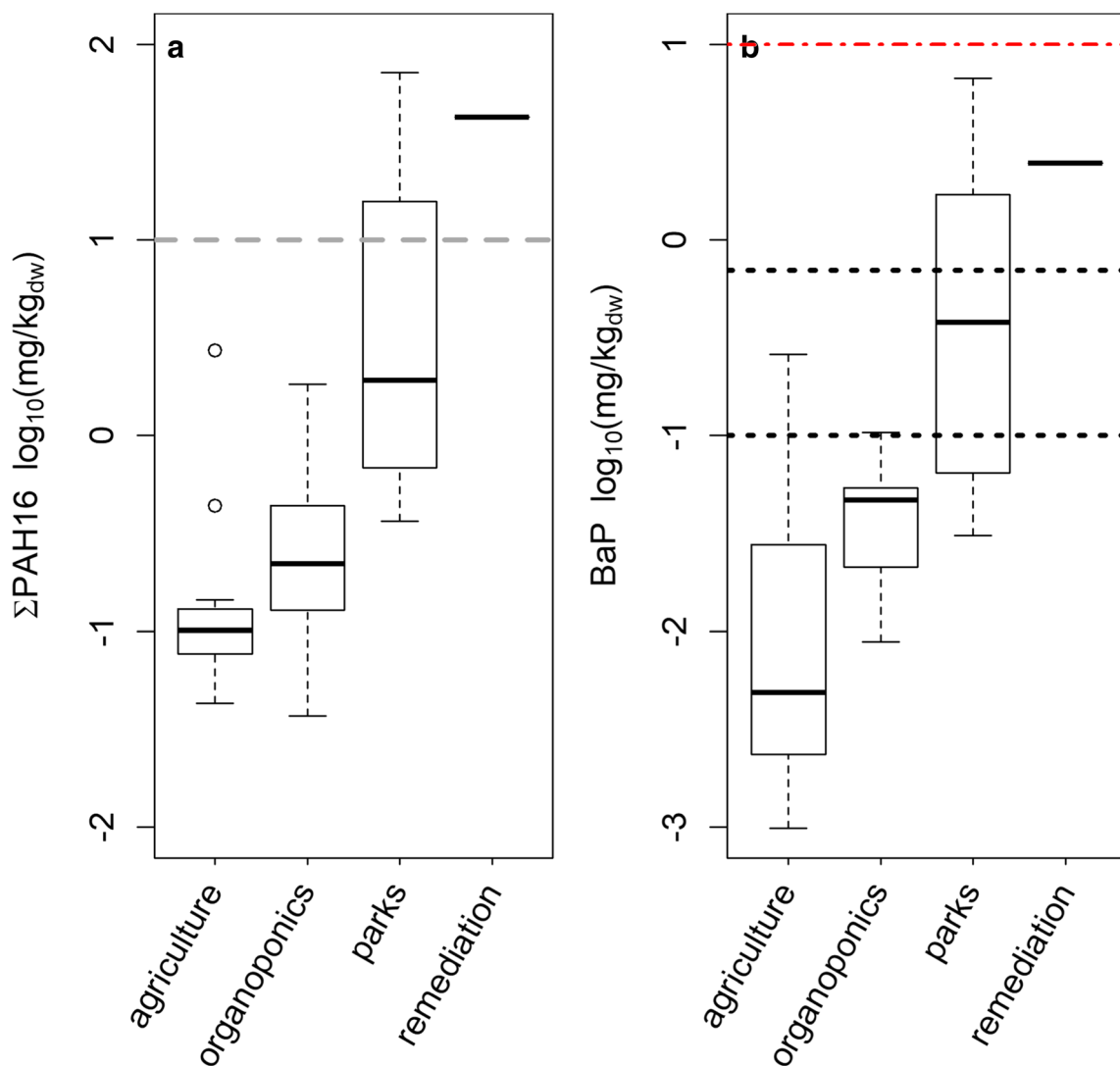


Fig. 2 The sum (Σ) of the polycyclic aromatic hydrocarbon (PAH16) concentrations (**a**) and benzo[*a*]pyrene (BaP) concentrations in Havana soils (**b**). The box represents the 25th to 75th percentile, the whiskers are the 10th and 90th percentile, and the dots are outliers. Twelve agricultural, eight organoponic, and seven park plots were measured and one remediation area (on-site bioremediation of an oil refinery). The dashed gray line in panel A indicates the Swiss trigger value for Σ PAH16 (VBBö 1998) of 10 mg/kg_{dry weight (dw)} (Table S1, Electronic Supplementary Material).

The two black dotted lines in **b** represent concentrations at 0.1 mg/kg_{dw} (Ecuadorian remediation value for agricultural soils, Table S1, Electronic Supplementary Material) and 0.7 mg/kg_{dw} (Ecuadorian remediation value for residential and industrial soils, Table S1, Electronic Supplementary Material), and the red dotted/dashed line at 10 mg/kg_{dw} (Ecuadorian and Mexican max. permissible value for commercial soils, Mexican max. permissible value for industrial soils and German action value for parks, Table S1, Electronic Supplementary Material)

compared to the Σ PAH16 concentrations in Havana parks (Fig. S1A, Electronic Supplementary Material). Thus, although PAH concentrations in Havana (park) soils are similar to other city soils, the contrast to the rural Mayabeque province is emphasizing the influence of the activity of humans in an urban area to the environment.

The land use (one factor with six groups according to Fig. S1A and S1B (Electronic Supplementary Material) but without the remediation site) in the ANOVA showed a significant influence (*p*-value: 0.003) on the PAH concentrations. However, only PAH concentrations in Havana agricultural

soils differed significantly from the capital’s park soils, parks, and industry sites from other soils around the world.

As Cuba has not yet regulated PAH concentrations in soil, BaP and Σ PAH16 results were compared with regulations of other countries (Fig. 2a, b, Table S1, Electronic Supplementary Material). The comparison with some European, North-, and Mesoamerican countries revealed that sites 4, 6, 8, and 10 (all park soils except 8 that is the remediation site) surpassed some RGV. If leaching of PAHs from soils into drinking water sources was considered also, the sites 2 (arable land), 3 (park), 4, 5 (park), 6, 8, and 10 are threats

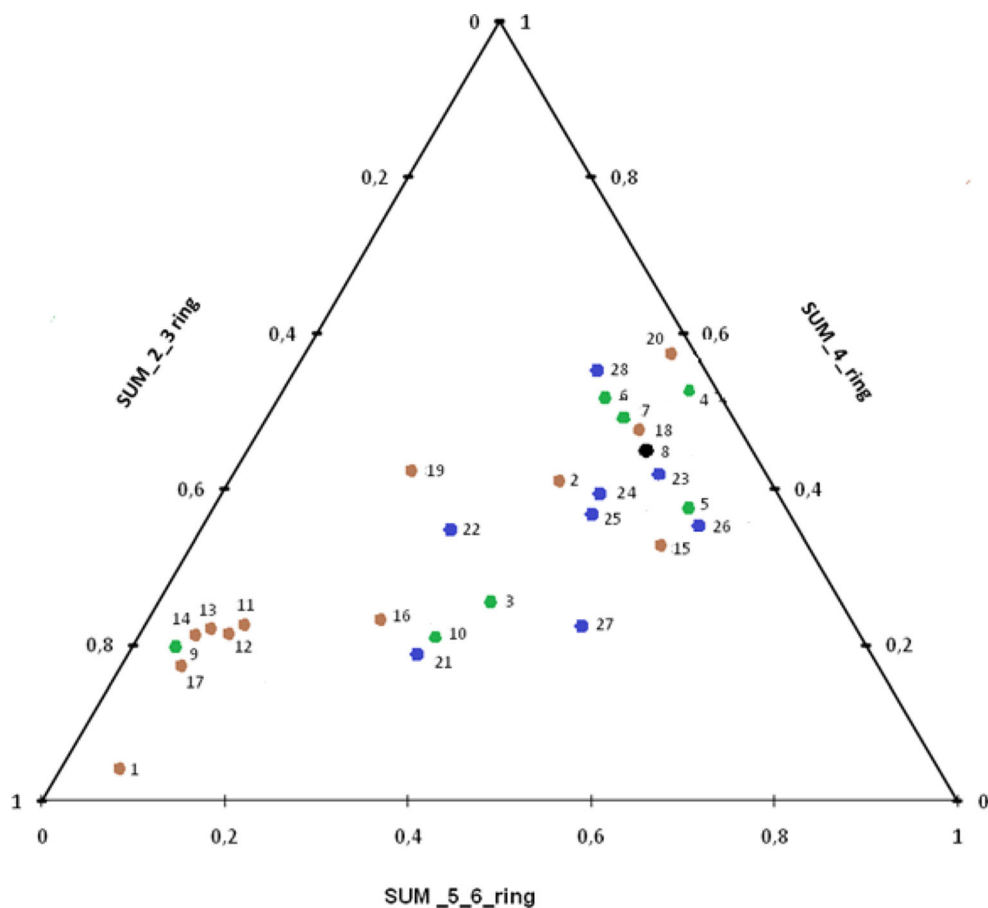
(Table S2, Electronic Supplementary Material). For further reading, we refer to chapter S1.

The fingerprint of the PAHs revealed predominance of NAP and PHE (2–3 ring PAHs) in arable soils with a contribution of 31 and 22% to the PAH16, respectively (Fig. 3, brown dots). These findings are in agreement with the results of other studies (Barra et al. 2007, Daly et al. 2007, Sosa et al. 2017, Wilcke 2007), where NAP and PHE dominated in soils with background PAH concentrations. Organoponics (Fig. 3, blue dots) tended to have a balanced fraction of all three ring groups, whereas park (green dots) soils rather were dominated by both, 4-ring and 5–6 ring PAHs. The prevalence of heavy (4-ring and 5–6 ring) PAHs is typical in urban areas with anthropogenic influence pattern (Wilcke 2007) and is due to (i) the lower volatilization of heavy PAHs from soils than of light compounds that are more prone to atmospheric transport, (ii) the predominance of fossil fuel combustion and biomass burning over petrogenic sources, and (iii) the tendency of heavier PAHs to accumulate in soils that are close to emission sources (Chung et al. 2007; Brändli et al. 2008; Liu et al. 2010; Agarwal and Bucheli 2011; Gubler et al. 2015). This outcome reflects the probable replacement of different climatic zones as major driver of PAH distribution pattern by an

anthropogenic impact through traffic, industry and agriculture.

To allocate the PAH's origin, the compounds in Fig. 3 were assigned to specific ratios that would indicate the source (Brändli et al. 2008). Indeed, BaA/(BaA&CHR) ratios showed combustion as the predominant process for most of the sites, and FLT/(FLT&PYR) and IPY/(IPY&BPE) specified it as petroleum combustion (Fig. S2, Electronic Supplementary Material) (Brändli et al. 2008). The outlier with an exceptionally low FLT/(FLT&PYR) is the park soil (site 10, 72 mg/kg Σ PAH16). The reason for this might be the close vicinity of this park to the oil industry refinery. The outlier on the right half of the graph with the highest FLT/(FLT&PYR) ratio (0.64) is site 20. The Σ PAH16 concentration is one of the lowest with 0.04 mg/kg with FLU (0.005 mg/kg) more than twice as high than PYR (0.002 mg/kg). The BPE concentration (6-ring) is associated with vehicle emissions, especially light-duty (Oliveira et al. 2011) as well as BaP that is usually emitted from catalyst and non-catalyst automobiles (Abe 2011). Indeed, the sum of 4–6-ring PAHs was higher than the sum of two and three ring PAHs when plotted against the Σ PAH16 (Fig. S3, Electronic Supplementary Material), which confirms fuel/Diesel

Fig. 3 Ternary plot of polycyclic aromatic hydrocarbons (PAHs) assorted by rings in Havana soils. The ring groups represent fractions of the sum of the PAH16 and are therefore unitless. Two and three ring PAHs are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene, 4-ring PAHs are fluoranthene, pyrene, benzo[*a*]-anthracene, chrysene, and 5–6 ring PAHs are benzo[*b*]-fluoranthene, benzo[*k*]-fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene. Brown dots represent agricultural sites, green are parks, blue are organoponics, and the black dot is the remediation area



combustion (BBodSchV 1999, Sosa et al. 2017) as the source of the PAHs. The BaP/BPE ratio was 0.9, which is also strongly suggesting that traffic is a predominant soil contamination source (Bucheli et al. 2004).

Finally, three potential emission sources (Fig. 1 and Table S2, Electronic Supplementary Material, A, smelter power plant, B, refinery power plant, C, thermoelectric power plant, incl. distances and sample number) were related with Σ PAH16 in samples from sites with increasing distance. The hypothesis was that with increasing distance the PAH concentrations will decrease. Indeed, this relation is discernible (Fig. S4, Electronic Supplementary Material), although with different coefficients of determinations. While a similar gradient but with lower PAH concentrations was observed in the Mayabeque province (Sosa et al. 2017), none of the regressions in the present study were significant. Reasons for this result might be that any gradient from the sources we hypothesize may be overridden by additional PAH emission sources not addressed here, such as biomass burning, coal combustion, and other industry emissions. Physico-chemical properties of the PAHs, rather than their emission sources, where light PAHs have lower degradation half-lives and volatilize better than heavy ones and heavy compounds therefore better reflect spatial relations (Gubler et al. 2015) might be responsible for this outcome as well.

3.2 PCB concentrations

The Σ PCB7 concentrations ranged from 2 to 100 $\mu\text{g}/\text{kg}$ (Fig. 4, Table S5, Electronic Supplementary Material). Agricultural plots exhibited lower concentrations (mean 10, median 2 $\mu\text{g}/\text{kg}$) than organoponic soils (mean 10, median 10 $\mu\text{g}/\text{kg}$) with the exception of an outlier showing a maximum at 0.1 mg/kg. According to Biasioli and Ajmone-Marsan (2007), park soils represent urban background conditions because these areas are less disturbed than other urban soils. However, in this study, the parks exhibited the highest concentrations (mean and median 20 $\mu\text{g}/\text{kg}$, each) except the maximum (60 $\mu\text{g}/\text{kg}$) which was lower than the one of arable land. While the median (2 $\mu\text{g}/\text{kg}$) and the minimum (1 $\mu\text{g}/\text{kg}$) of the Σ PCB7 in the Mayabeque study (Sosa et al. 2017) were comparable with the concentrations of arable land in Havana city, the maximum concentration (10 $\mu\text{g}/\text{kg}$) was clearly lower in the rural than the capital area. Havana park concentrations (Fig. S5A, Electronic Supplementary Material) were similar to the PCB contamination of parks of several other cities (Fig. S5B; Motelay-Massei et al. 2004, Shelepchikov et al. 2011, Wong et al. 2009). In contrast, PCB concentrations in agricultural soils of other studies (Wilcke et al. 1999a; Wang et al. 2010; Lopez et al. 2011; Witzak and Abdel-Gawad 2012; Antolín-Rodríguez et al. 2016; Kim et al. 2016; Halfadji et al. 2017; Pokhrel et al. 2018) were significantly lower than the ones in corresponding soils of this study

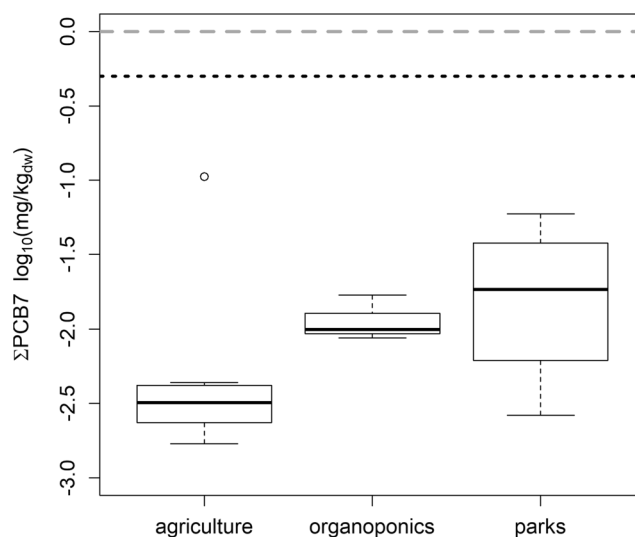


Fig. 4 The sum (Σ) of the seven indicator polychlorinated biphenyl (PCB7) concentrations of Havana soils. The box represents the 25th to 75th percentile, the whiskers are the 10th and 90th percentile, and the dots are outliers. There are 12 agricultural, eight organoponic, and seven park soils. The dotted line represents the 0.5 mg/kg Σ PCBs maximally allowable value according the Cuban regulation and the remediation value of Ecuador, the max. contamination value of Mexico, and the soil quality guideline value of environmental protection of Canada (Table S1, Electronic Supplementary Material). These values are for agricultural soils. The gray dashed line is the 1 mg/kg_{dry weight (dw)} Σ PCB7 remediation value of parks in Switzerland (Table S1, Electronic Supplementary Material)

(Fig. S5, Electronic Supplementary Material). Although the PCB concentrations of the single industrial site in this study, the petroleum remediation area was not determined, the PCB concentrations from industrial sites of other studies (Nadal et al. 2011; Shelepchikov et al. 2011; Vane et al. 2014; Halfadji et al. 2017; Pokhrel et al. 2018) are depicted in Fig. S5B (Electronic Supplementary Material) for reasons of comparison. The land use had a significant influence (ANOVA, p -value $6.3e-12$) on the PCB concentrations. In summary, PCB concentrations in organoponic and park soils of Havana city corresponded to park soils of other cities in the world and were significantly lower than industrial sites but significantly higher than agricultural soils with urban influence.

From a regulator point of view, the PCB concentrations in Havana were at least one order of magnitude below 0.5 mg/kg Σ PCBs (dotted line in Fig. 4), representing the maximum allowable value in Cuba, the remediation value of Ecuador for agricultural soils, the maximum contamination value of Mexico for agricultural soils, and the soil quality guidelines for environmental protection (SQG_E) of Canada for arable land (Table S1, Electronic Supplementary Material). The gray dashed line (Fig. 4) is the 1 mg/kg Σ PCB7 remediation value of parks in Switzerland (Table S1, Electronic Supplementary Material) that is obviously higher than the threshold values for agricultural soils.

PCB homolog group profiles resulted in a major concentration contribution of hexa-chlorinated (C16)-PCBs (#138, #153) with a mean of 47%, followed by hepta-chlorinated (C17)-PCBs (#180) with 19%, tetra-chlorinated (C14)-PCBs (#52, #101) with 18%, and tri- (C13)- and penta-(C15) chlorinated PCBs (#28, #118) with a mean contribution of 14%, each (Table S6, Electronic Supplementary Material) in Havana soils. Most of the C16- and C17-PCBs predominated around the refinery and the thermoelectric power plants (Fig. 1, points B and C, Table S2, Electronic Supplementary Material). The C16- and C15- or the C16- and C13-PCBs were most abundant near the smelter power plant (Fig. 1, point A, Table S2, Electronic Supplementary Material). Several reasons could be responsible for this finding. Firstly, low molecular weight (LMW) or rather less chlorinated PCBs (C13 and C14) tend to volatilize from soil, while high molecular weight (HMW)/highly chlorinated PCBs (C16 and C17) deposit into the soil (Cetin et al. 2017). Secondly, with increasing chlorination of biphenyls, degradation rates by aerobic bacteria typically present in air pockets of non-water-saturated natural soils decreases (Borja et al. 2005; Field and Sierra-Alvarez 2008). Field and Sierra-Alvarez (2008) reported of natural dichlorobiphenyl degrading strains, but as the chlorination increased, less and less strains were able to metabolize the PCBs, which is expressed in the persistency of these compounds as outlined earlier.

The congener frequency (means of 23% for #153, 24% #138, 19% for #180) in this study was very similar to the one found in the Mayabeque study (means of 26% for #153, 16% #138, 15% for #180) (Sosa et al. 2017). Similar to the outcome in Sosa et al. (2017), the relative low abundance of, e.g., #28 (10%), #118 (13%) was not in accordance with PCB fingerprints in transformer oils that dominated in the Cuban inventory (Abo Balanza 2005). There, 90% of Sovol consists of C13- and C15 chlorinated PCBs with 10% C13-PCBs, which renders the product to Sovtol (Treger 2012) that was mainly found in industry plants (Abo Balanza 2005).

To assess any pattern of the land use and the PCB congeners, a PCA was run with the PCBs that were measured most frequently, which were the congeners #101, #118, #153, and #138 measured at 23 sites (Fig. 5). The two principal components (PC) explained 96% of the variance (93% by PC1 and 5% by PC2). On the left side of the vertical 0-line are almost all agricultural sites. These soils have higher fractions of C14 and C15 than park soils or organoponics. On the right hand side of the vertical 0-line are the sites with the highest fractions of C16 (#153, #138). The vectors in the biplot (Fig. 5) are long, which indicates a strong influence. All PCBs correlate positively with each other but the two C16 congeners correlate highly. So, PC2 discriminates the individual congeners along the horizontal 0-line. All organoponics are on the lower half of the biplot except site 27. They have the highest #153 fractions ranging from 29 to 39% (site 27 has 26%) in comparison to

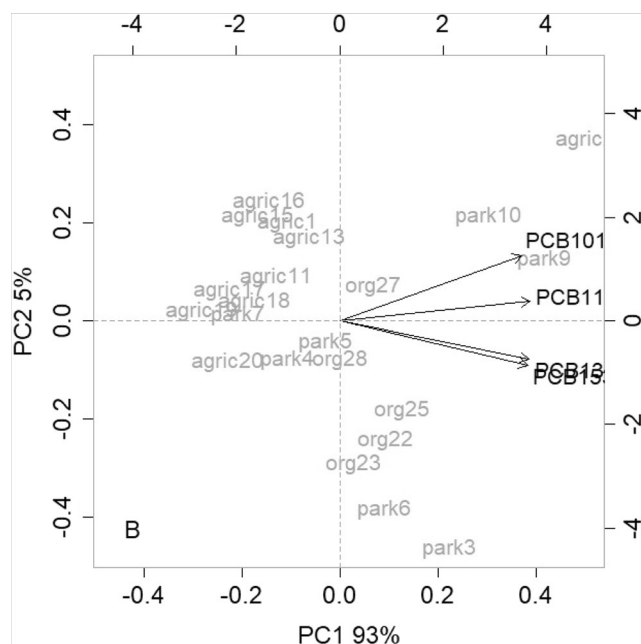
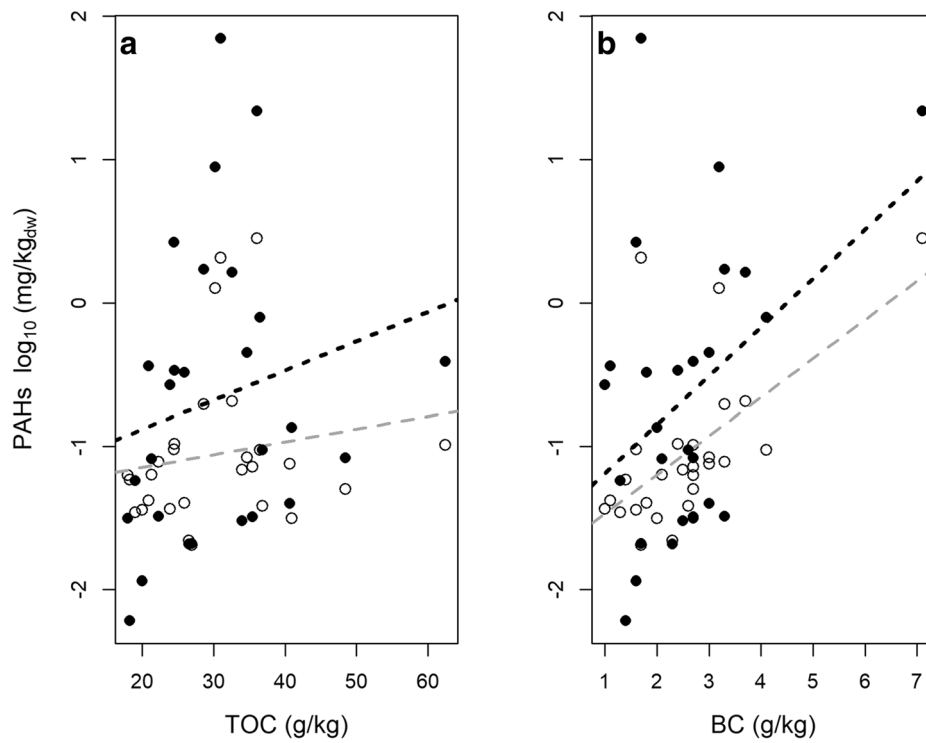


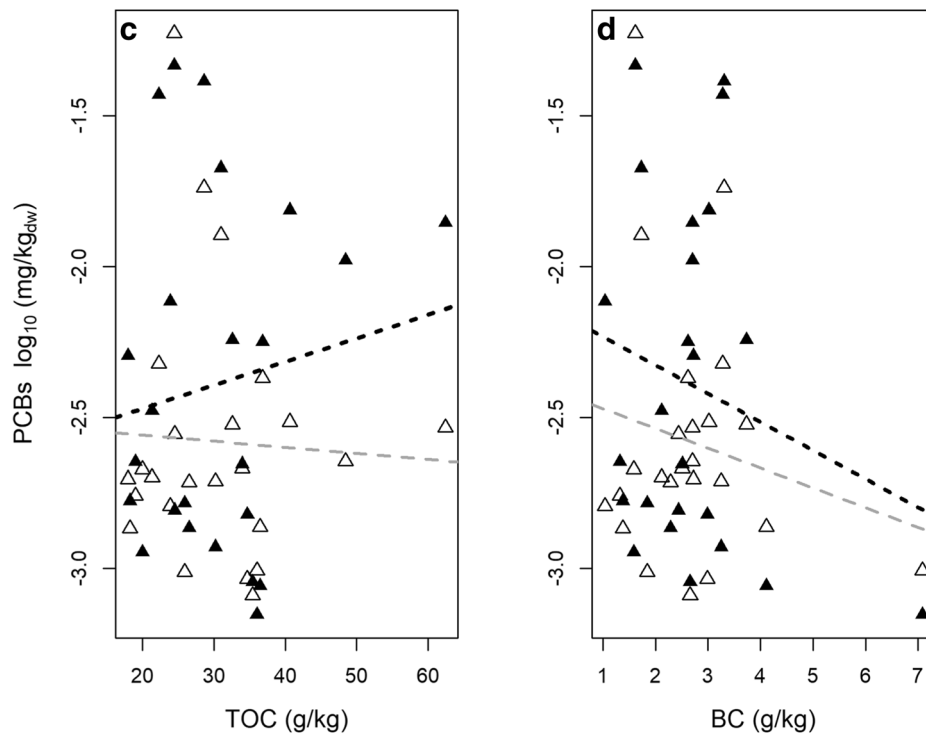
Fig. 5 Loadings (%) of the first two principal components (PC) derived by a PC analysis based on log-transformed data. The four congeners that were found in most of the sites (23) are depicted in the panel. The upper x- and the right y-axis refer to the scores of the vectors (arrows) and the lower x- and the left y-axis are the scores of the observations. The vectors represent the PCB congeners #101, #118, #153, and #138 and their length represents the maximized variance. The distance between two observations represents the Euclidean distance (Kohler and Luniak 2005). The abbreviations of the cases correspond to the land use (agric = agriculture, org = organoponic, park = park). The numbers in the cases correspond to the survey site description (Table S2, Electronic Supplementary Material)

agricultural soils. Park soils are distributed all over the biplot. Park 9 has the highest #138 fraction (32%) and parks 7 and 4 the lowest (23%) in comparison to all other park soils. The reason for this dispersion over the biplot may be that the Σ PCB4 contribution is lowest in park soils in comparison to the organoponics and the arable land. Park soils had the highest #180 fractions ranging from 11 to 33%. In contrast, most of the arable land showed no detections of the C17 compound (Table S6, Electronic Supplementary Material).

Hexa-chlorinated PCBs prevailed not only in Havana but also elsewhere over the world as for instance in Chinese urban surface soils including Shanghai (Hammes et al. 2007), in urban sites of the Seine Basin, France (Motelay-Massei et al. 2004; Jiang et al. 2011), and in the region of Estarreja, Portugal (Cachada et al. 2012). However, the homolog group dominating in urban soils of Bursa, Turkey was the C15- (29%), C14- (26%), and C13- (18%) chlorinated PCBs (Breivik et al. 2002). Breivik et al. (2002) reported that 70% of the PCBs produced globally were C13-, C14-, and C15-PCBs, which is also representative for the Cuban inventory results. Tetra- and penta- and fewer hexa-chlorinated PCBs had the major contribution to the sum of the PCBs in urban and peri-urban soils in central and Eastern Europe (Wilcke et al. 2006). The principal PCB homolog group in global



○ 2-3 ring PAHs
 ● 4-6 ring PAHs
 - - lin. regr. 2-3 ring PAHs
 - · - lin. regr. 4-6 ring PAHs



△ C13, C14, C15
 ▲ C16, C17
 - - lin. regr. C13, C14, C15
 - · - lin. regr. C16-, C17

◀ **Fig. 6** Polycyclic aromatic hydrocarbon (PAHs, **a** and **b**) and polychlorinated biphenyl (PCBs, **c** and **d**) concentrations versus total organic carbon (TOC) and black carbon (BC) concentrations in Havana soils. Abbreviations: lin. regr.: linear regression; C13: trichlorinated PCB; C14: tetrachlorinated PCB; C15: pentachlorinated PCB; C16: hexachlorinated PCB; C17: heptachlorinated PCB, dw: dry weight. The *p*-values of the lin. regr. were not significant except for the PAHs in dependence of the BC (**b**, 2–3 ring PAHs: *p*-value = 0.0008, $R^2 = 0.36$; 4–6 ring PAHs: *p*-value = 0.03, $R^2 = 0.16$)

background contaminated soil has been reported as C16- (46%) followed by C15-PCBs (27%) (Meijer et al. 2003). Hence, not only urban or rural influences shape PCB profiles but also their use in the past, their production then and now, and their emissions into the environment (Li et al. 2011).

3.3 Relation between TOC, BC, and PAH, PCB concentrations in soil

The concentration of TOC and BC ranged from 18.0 to 135.9 g/kg, and from 1.1 to 7.9 g/kg, respectively (Table S7, Electronic Supplementary Material). The mean concentration of TOC (34.2 g/kg) and BC (2.7 g/kg) in the soils of Havana was higher than in the rural Mayabeque (mean TOC 26.2 g/kg and BC 1.6 g/kg) (Sosa et al. 2017). The soil of the remediation area (site 8) presented the highest value of TOC (135.9 g/kg) and BC (7.9 g/kg), which can be explained with the petroleum residues in the soil used to clean of the crude oil tanks. The minimum, maximum, and median BC/TOC ratio were 0.04, 0.11, and 0.07, respectively, and were higher than those from the rural soils of Mayabeque (0.01, 0.03, and 0.06, respectively) (Sosa et al. 2017). In international comparison the BC in the Havana soils was above the concentrations found in Swiss soils (0.4 to 4.8 g/kg (Agarwal and Bucheli 2011)), and the BC/TOC ratio was a little higher (median 0.04) than the value compiled in a review of Cornelissen et al. (2005) with 90 soil sites.

In general, organic pollutants, such as PAHs and PCBs, strongly interact with soil organic matter (Meijer et al. 2002, 2003; Jiang et al. 2011, Gai et al. 2014) due to the high K_{OC} values (Panagopoulos et al. 2017; Bartolomé et al. 2018). Some authors noted that PAHs were not significantly influenced by TOC concentrations until it arrived at a certain level in weakly polluted soils with total PAH concentration > 2 mg/kg (Simpson et al. 1996; Zhang et al. 2006).

Cetin et al. (2017) suggested from a fugacity model that soils tend to be a source for LMW PAHs and PCBs and a sink for their HMW compounds. Therefore, we divided the PAHs into LMW (2–3 rings) and HMW (4–6 rings) and the PCBs into LMW (C13-, C14-, C15-) and HMW (C16-, C17-) congeners and plotted their concentrations separately against the TOC and BC concentrations, respectively (Fig. 6; site 8 was excluded from the regressions because it contains extraordinary high TOC and BC concentrations and is therefore an

outlier). The hypothesis was to find a relationship between the HMW PAHs or HMW PCBs but not so for the LMW compounds.

The linear relationship between the TOC in soil and the PAHs was weak and between the BC and PAHs better and significant (Fig. 6a, R^2 of the lin. regr. if plotted against TOC was 0.03 and 0.04 for LMW and HMW PAHs, respectively; Fig. 6b, R^2 of the lin. regr. if plotted against BC was 0.36 (*p*-value 0.0008) and 0.17 (*p*-value 0.03), respectively, for the LMW and HMW PAHs. Indeed, BC was considered to play a major role in distribution of PAHs in soil due to their co-emission and high sorption capacity for PAHs (Agarwal and Bucheli 2011). In both plots (Fig. 6a, b), HMW PAHs showed a steeper slope than LMW PAHs, which might confirm the hypothesis of preferential volatilization of LMW compounds. A lack of correlation or even a counterintuitive trend was observed for the TOC and BC versus PCB concentrations (Fig. 6c, d). This is surprising as Sosa et al. (2017) found a good correlation of the PCB7 and BC in the soils of Mayabeque province, Cuba. Also, other researchers found good correlations between TOC and > C15 PCBs (Wilcke et al. 1999a; Heywood et al. 2006). However, other studies did also not find a good correlation between PCBs and TOC (Klánová et al. 2008, Wilcke et al. 2006). It might be that not only the distribution equilibrium between the PCBs in the Havana province soils and their BC but also TOC concentrations were not reached due to the constant change/load of the contaminants (including BC) in the highly dynamic urban environment. Or, that the missing relation between the organic pollutants and BC is due to the methodology employed for the BC quantification that is selective for soot-like BC (Agarwal and Bucheli 2011) and does not quantify char-like BC (Hammes et al. 2007). In summary, the relationship suggested by the fugacity model of Cetin et al. (2017) could not be found in this study for PCBs.

4 Conclusions

In summary, PAH concentrations in agricultural and organoponic soils from Havana were comparable with agricultural soils from other studies. Parks and organoponic sites of Havana showed a similar concentration range as parks and industry sites of the rest of the world. However, when the risk to human and environmental health and the different pathways of exposure are considered (Canadian SQG_E), some public parks pose a risk concerning PAHs to people when having direct contact but not so, if they ate some food products from these sites. PCB concentrations in Havana agricultural and organoponic soils were significantly higher than in agricultural and industrial soils of other studies, while parks of both, Havana and the rest of the world were in the same range. The PCBs in Havana soils were far below any threshold values

suggested by some American countries or Europe irrespective of the land use.

Lower PAH concentrations in the rural Mayabeque in comparison to the urban Havana were clearly discernible, in line with the general notion that urban development causes increased environmental impact. To observe the development of organic pollutants due to human activity on environmental concentrations, the soil monitoring network that has just started with the sampling of the Havana and Mayabeque soils will expand and maintain their periodical sampling campaigns. Soil sampling in other provinces all over the country with regular time intervals of for instance five years will provide the necessary information whether environmental impacts will increase or fall with increasing GDP. The data will be communicated to the Ministry of Science, Technology, and Environment of Havana City and form part of the information necessary to establish RGV for PAH values in soils in Cuba. The PCB concentrations do not only update the country's PCB contamination status but also provide important information on the progress of the worldwide POPs distribution and abatement.

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