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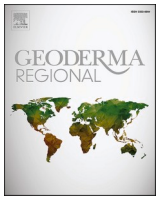

Polycyclic aromatic hydrocarbons concentration and spatial distribution in the soils of Santiago de Compostela (northwestern Spain)

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ABSTRACT

Organic pollutants are commonly accumulated in urban soils, interfering with the normal functions of soils and ecosystems, and representing potential risks for human health and well-being. Here we have studied the presence of polycyclic aromatic hydrocarbons (PAHs) in 55 soils from the city of Santiago de Compostela (Spain). The soils include different land uses: urban grasslands, urban forests, urban and periurban agricultural soils. Sample preparation was carried out by miniaturized ultrasound-assisted extraction and analytical determination was performed by gas chromatography-tandem mass spectrometry. Results revealed the presence in the soils of 17 out of the 18 PAHs analyzed, with total concentration levels up to μg g^{-1} in 28% of the analyzed soils. The sum of their concentrations varied widely, between 4 and 4728 ng g^{-1}, with a mean value of 508 ng g^{-1} (median 217 ng g^{-1}). The sum of the 16 EPA PAHs ranged from 4 to 4216 ng g^{-1}, with a median of 193 ng g^{-1}. The values found are similar to other similar-sized cities with low population densities. The study of PAHs distribution with depth in one soil showed that these compounds are mainly concentrated in the top 20 cm. Spatial distribution was very heterogeneous and without a clear pattern. In general, all PAHs were strongly intercorrelated except naphthalene, whereas no correlations have been found to soil physicochemical properties. Strong correlation of PAHs with Pb was observed, suggesting a common major source for these pollutants, probably combustion by traffic and households.

1. Introduction

Urban soils play relevant functions in the ecosystems of our cities, functions that are important for building inclusive, safe, resilient and sustainable cities, as recognized in Goal 11 of the UN 2030 Agenda Sustainable Development Goals (Morel et al., 2015; Lal et al., 2021). However, these functions can be negatively affected by the widespread presence of contaminants in urban areas, in particular those more directly related to plant production or habitat for biodiversity, due to the presence of diverse sources of pollution near or within the cities (industrial facilities, traffic, urban waste treatment and disposal, coal combustion…). Many of these contaminants end up accumulating in urban soils that, as a result, are commonly polluted by organic and inorganic substances (Ajmone-Marsan and Biasioli, 2010; Li et al., 2018), in many cases from historical pollution processes. Besides, contaminants can be mobilized from soil towards other compartments of the environment, so their transference from and to the soil is an important issue that needs to be studied, in especial when they reach the waters or enter the food chain. In this sense, the presence and location of contaminants in urban soils is one of the most studied aspects of urban soil properties and must be clearly established to ensure safe land uses.

Polycyclic aromatic hydrocarbons (PAHs) are among the most characteristic pollutants in urban areas, and in fact they are typical markers of urban pollution. The main sources of PAHs include motor vehicle exhaust, industrial activities, coal and biomass combustion, and atmospheric deposition of long-range transported PAHs. Soils are a well-known sink for PAHs, where they accumulate because they are strongly retained by the components of the solid phase of soil (Wilcke, 2000; Tsibart and Genadiev, 2013). Because of their low polarity, high lipophilicity and no electrical charge, which result in low water solubility

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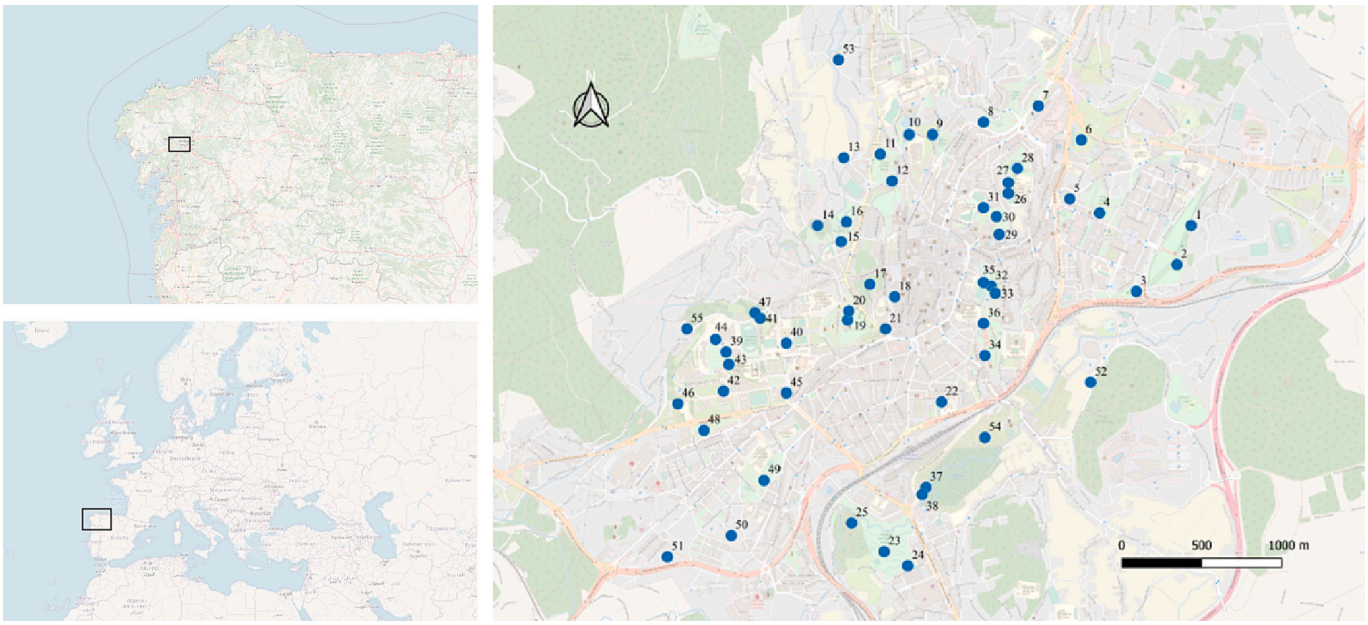

Fig. 1. Location of study area and sampling points.

and high affinity for soil solid components, when PAHs reach the soil mainly from atmospheric deposition, they tend to accumulate. Thus, the PAHs present in urban soils usually reflect centuries of habitation or the legacy of industrial activities; besides, the increases in urban population and traffic and associated activities in recent times have also resulted in new sources of PAHs accumulating in urban soils (Peng et al., 2013).

Studies on PAHs concentrations have been performed in many cities in the world, as reviewed by Li et al. (2018), with a dominant interest in densely populated urban areas in China (Gao et al., 2019; Zhang et al., 2022; Xu et al., 2023). Preference for more industrialized and populated cities, where chances to find high pollution levels are higher, has concentrated research efforts so far, so knowledge gaps still exist in what concerns world regions and city typologies. In this sense, as recently highlighted by Gao et al. (2019), PAHs concentration in urban soils of small cities have been less studied than in high, industrialized/polluted cities, although they are equally important. In addition, reports of organic pollutant concentrations in urban soils in Spanish cities are still scarce. With the objective of contributing information about urban soil contamination in Spain, in this work we have studied the presence of PAHs in the soils of the city of Santiago de Compostela (northwestern Spain). This work is part of a wider ongoing project on the urban soils in this city, where several aspects of their properties and functions are being studied, including soil types (Paradelo et al., 2022), general chemical properties (Paradelo et al., 2021), presence of trace metals (Herbón et al., 2021) or microbiology (Gómez-Brandón et al., 2022; Probst et al., 2023). The specific aim is to complete information on pollution status on these soils, which until now is limited to inorganic pollutants. Soils in this city will likely present lower PAHs pollution than soils in more industrialized and densely populated cities, but information on their concentrations and spatial distribution is important for planning of land uses in the city, in particular in what refers to urban agriculture projects.

2. Material and methods

2.1. Study area

The city of Santiago de Compostela, with an area of 222 km^2 and 97,000 inhabitants, is the capital of the region of Galicia (NW Spain) and an important political, administrative, religious and tourist center. It has a warm and wet climate, classified as temperate oceanic (Cfb) according to the Köppen–Geiger Climate Classification (Kottek et al., 2006). The mean annual air temperature of 13.0 °C, with August as the warmest month (mean air temperature 19 °C). and January the coldest (mean air temperature 8 °C). The average annual precipitation is 1787 mm. The city is in the contact zone between a granitic area and the Santiago Unit of the metamorphic massif known as the Ordes Complex, with presence of four main lithologies: granitic rocks, schists, orthogneisses and amphibolites. The soils present in the green areas studied in this work would be classified as Leptic Umbrisols, Haplic Umbrisols, Skeletic Regosols and Urbic Technosols (IUSS Working group-WRB, 2014; Paradelo et al., 2022).

Table 1
Summary of soil properties. OC: total organic carbon; CEC: cation exchange capacity.

		pH	OC (g kg^{-1})	Clay (g kg^{-1})	CEC (cmol$_c$ kg^{-1})
Urban grasslands	*range*	5.0–6.3	13–70	93–309	9–22
	mean ± *sd*	5.6 ± 0.3	33 ± 12	149 ± 41	16 ± 3
Urban forests	*range*	4.7–6.5	21–110	107–245	11–36
	mean ± *sd*	5.4 ± 0.5	44 ± 24	150 ± 37	19 ± 7
Urban and periurban agriculture	*range*	5.5–6.9	21–49	111–248	12–31
	mean ± *sd*	6.1 ± 0.4	35 ± 9	156 ± 40	17 ± 4

2.2. Soils

We analyzed urban soils sampled at 55 points in green areas of the city of Santiago de Compostela (Fig. 1), over several parent materials and under different vegetation types and land uses (Table S1). A total of 28 samples in urban grasslands, 13 in urban forests and 14 in urban and periurban agricultural areas, have been analyzed. Composite samples (soil depth 0–5 cm) were taken with an auger by mixing 4–5 subsamples at each point. In addition, PAHs were analyzed at different depths in one point (soil 21), divided in the following depth fractions: 0–5, 5–10, 10–20, 20–30, 30–40, 40–50 and 50–70 cm. A summary of the main

properties of the soils is shown in Table 1: soils are in general acid, rich in organic matter, with medium to coarse textures, dominated by sandy loams. Additional data characterization of the soils can be found in previous publications (Paradelo et al., 2021; Gómez-Brandón et al., 2022; Herbón et al., 2021).

2.3. Reagents and materials

The PAHs analyzed, their CAS numbers, retention times and MS/MS transitions are summarized in Table S2. The 16 EPA PAHs mixture solution (2000 μg mL^{-1}) was provided by Supelco (Bellefonde, USA), and B[*j*]F (2,000 μg mL^{-1}) and B[*e*]P (100 μg $mL^{-}1$) were provided by Sigma-Aldrich. 2,4,6-trichlorobiphenyl (PCB-30), supplied by Dr. Ehrenstorfer (Augsburg, Germany), was employed as internal standard. Stock solutions were prepared in ethyl acetate. Further dilutions and mixtures were prepared in acetone (spike solutions) or ethyl acetate (calibration studies), provided by Sigma-Aldrich (Steinheim, Germany). Stock solutions were stored in glass vials protected from light at −20 °C. All reagents were of analytical grade.

2.4. PAHs extraction and analysis

PAHs extraction was performed by miniaturized ultrasound-assisted extraction (UAE). The experimental conditions were adapted from those previously optimized (Celeiro et al., 2018). Briefly, 200 mg of soil were placed in a glass vial, the internal standard PCB-30 (10 μL of an acetonic solution at 10 μg mL^{-1}) and 2 mL of ethyl acetate were added, and the vial was sealed with an aluminum cap furnished with PTFE-faced septum. Vials were immersed into an ultrasound bath (*P. Selecta*, Barcelona, Spain) for 10 min, at 50 kHz and controlled temperature (25–30 °C). After extraction, the organic supernatant was filtered through 0.22-μm PTFE filters before its GC–MS/MS analysis. For recovery studies, 10 μL of an acetonic solution containing the 18 target PAHs at 0.1 μg mL^{-1} and 1 μg mL^{-1} were added to a soil sample, to obtain spike levels of 5 ng g^{-1} and 50 ng g^{-1}, respectively. The GC–MS/MS analyses were performed on a Thermo Scientific Trace 1310 gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 8000) with an autosampler IL 1310 from Thermo Scientific (San Jose, CA, USA). Separation was performed employing a Zebron ZB-Semivolatiles (30 m × 0.25 mm i.d. × 0.25 μm film thickness) column provided by Phenomenex (Torrance, CA, USA). Helium (purity 99.999%) was employed as carrier gas at a constant flow of 1.0 mL min^{-1}. The GC oven temperature was programmed from 60 °C (held 2 min) to 210 °C at 15 °C min^{-1} and to 290 °C at 5 °C min^{-1} (held 5.5 min). The total run time was 33 min. Pulsed splitless mode (200 kPa, held 1.2 min) was employed for injection. The injector temperature was set at 270 °C, and the injection volume was 1 μL. The mass spectrometer detector (MSD) was operated in the electron ionization (EI) positive mode (+70 eV). The temperatures of the transfer line and the ion source were set at 290 °C, and 350 °C, respectively. Selected Reaction Monitoring (SRM) acquisition mode was implemented monitoring 2 or 3 transitions per compound (see Table S2), for an unequivocal identification and quantification of the target compounds. The system was operated by Xcalibur 2.2, and Trace Finder™ 3.2 software. Retention times as well as the quantification and identification MS/MS transitions (eV) are also included in the Table S2.

2.5. UAE-GC–MS/MS performance

Results of the UAE-GC–MS/MS method performance, evaluated in terms of linearity, precision, accuracy, relative standard deviation (RSD) values for 100 μg L^{-1} and limits of detection (LOD), are summarized in Table S3. Calibration studies were performed employing standard solutions prepared in ethyl acetate containing the 18 target PAHs, covering a concentration range from 0.1 to 1000 μg L^{-1}. Precision was evaluated within a day ($n = 3$) and among days ($n = 6$) at the different

Table 2
Summary of PAH concentrations in the soils (ng g^{-1}) and results of one-way analysis of variance for influence of land use. Abbreviations: Nap – naphthalene, Acy – acenaphthylene, Ace – acenaphthene, Flu - fluorene, Phen - phenantrene, Anc - anthracene, Fla. - fluoranthene, Pyr - pyrene, B[*a*]A - benzo(*a*)anthracene, Chy - chrysene, B[*b*]F - benzo(*b*)fluoranthene, B[*j*]F - benzo(*j*)fluoranthene, B[*k*]F benzo(*k*)fluoranthene, B[*e*]P - benzo(*e*)pyrene, B[*a*]P - benzo(*a*)pyrene, Ind - Indene[1,2,3-*cd*]pyrene, D[*ah*]A - dibenzo(*a,h*)anthracene, B[*ghi*]P - benzo(*g,h,i*)perylene, BaPeq - benzo(*a*)pyrene equivalent concentration.

	Nap	Acy	Ace	Flu	Phen	Anc	Fla	Pyr	B[*a*]A	Chy	B[*b*]F + B[*j*]F	B[*k*]F	B[*e*]P	B[*a*]P	Ind	D[*ah*]A	B[*ghi*]P	∑PAHs	∑16 EPA	BaPeq
Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*4*	*4*	*0.004*
Maximum	*97*	*56*	*23*	*17*	*219*	*71*	*779*	*603*	*386*	*667*	*406*	*196*	*551*	*391*	*297*	–	*274*	*4728*	*4216*	*489*
Mean	*7.4*	*2.1*	*1.6*	*1.8*	*27.1*	*5.2*	*72.8*	*58.2*	*39.1*	*59.7*	*42.0*	*22.9*	*62.1*	*43.1*	*30.7*	–	*32.0*	*508*	*458*	*54.6*
Median	*3.1*	*0.0*	*0.7*	*0.8*	*11.0*	*2.0*	*26.5*	*22.0*	*15.5*	*23.0*	*17.0*	*9.5*	*27.8*	*15.0*	*12.5*	–	*14.5*	*217*	*193*	*19.7*
SD	*15*	*8*	*3*	*3*	*44*	*12*	*136*	*105*	*68*	*121*	*75*	*38*	*105*	*77*	*56*	–	*51*	*894*	*788*	*97*
% Det. freq.	*82*	*21*	*75*	*66*	*93*	*66*	*100*	*100*	*88*	*95*	*89*	*84*	*95*	*89*	*82*	*0*	*89*	–	–	–
ANOVA																				
Land use - F	*0.7*	*1.1*	*0.1*	*0.4*	*0.7*	*1.0*	*1.0*	*1.0*	*1.0*	*1.8*	*1.7*	*1.4*	*1.4*	*1.2*	*1.6*	–	*1.4*	*1.2*	*1.1*	*1.3*
p	*0.5*	*0.4*	*1.0*	*0.7*	*0.6*	*0.4*	*0.4*	*0.4*	*0.4*	*0.2*	*0.2*	*0.3*	*0.2*	*0.3*	*0.2*	–	*0.3*	*0.3*	*0.4*	*0.3*

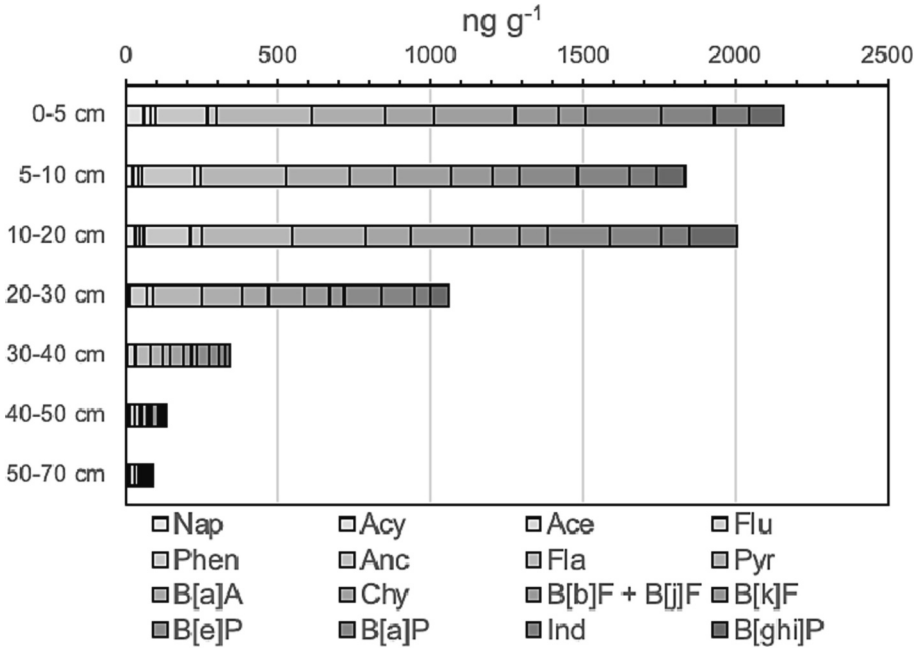

Fig. 2. PAHs concentrations at different depths in soil 21. See Table 2 for abbreviations.

concentration levels. Accuracy was evaluated by recovery studies employing two real soil samples at two fortification levels: 5 and 50 ng g^{-1}. The initial PAHs concentrations in these samples were taken into account. Recoveries were calculated by comparing the chromatographic response (area counts) between the spiked samples after UAE-GC–MS/MS analysis and standards prepared in ethyl acetate containing the 18 target PAHs, after GC–MS/MS analysis. The limits of detection (LODs) of the method were calculated as the compound concentration giving a signal-to-noise ratio of three (S/N = 3), excluding NAP, since this compound was detected in the procedure blanks. In this case, its LOD was estimated as the average amount of analyte giving a response in the blank plus 3 times the standard deviation.

2.6. Risk assessment

The toxicity equivalency factor (TEF), developed by the U.S.EPA to assess the risks of a mixture of structurally related chemical compounds (U.S. EPA, 2008), was calculated. It is based on the relative toxicity of each chemical compared to a reference compound, which for PAHs is benzo(*a*)pyrene. This reference compound is assigned a TEF of 1, while the other chemicals are assigned TEFs that are order-of-magnitude estimates of potency. The values employed here, compiled from different sources (Bull and Collins, 2013; Jiang et al., 2016; Cetin, 2016; Santos et al., 2017), are the following: 1 for B(*a*)P and D(*a*,*h*)A, 0.1 for B(*a*)A, B(*k*)F and indene, 0.01 for anthracene, chrysene, B(*e*)P, B(*b*)F, B(*j*)F and B(*g*,*h*,*i*)P, and 0.001 for the rest of compounds. To calculate the benzo(*a*)pyrene equivalent concentration (BaPeq), the concentration of the individual chemical (Ch) is multiplied by its TEF value:

$$\text{BaPeq} = \Sigma\,(\text{Ch}\cdot\text{TEF})$$

2.7. Statistics

One-way ANOVA was used to determine the influence of land use on soil PAH concentrations. Before analysis, the normality of data was checked using the Shapiro-Wilk test. Data that did not pass the normality test were log-transformed for ANOVA. The homogeneity of variance was tested using the Levene test. When a significant effect of land use at a level of significance of $P < 0.05$ was found, the Tukey's multiple range test was used to separate groups. Pearson's correlation analyses between all the soil properties analyzed were also conducted. Principal component analysis (PCA) was employed for the characterization of the relation between soil physicochemical properties and contaminant concentrations. This analysis was conducted using the R packages *factoextra* (Kassambara and Mundt, 2017) and *FactoMineR* (Lê et al., 2008). All statistical analyses were performed using the R statistical package for MacOSX version R 3.1.3 (R Core Team, 2018) and the package R Commander version 2.6–1 (Fox and Bouchet-Valat, 2019).

3. Results and discussion

Table 2 shows a summary of the concentrations of the 18 PAHs analyzed in the 55 surface soil samples (full data for each individual soil are included in the supplementary material, Table S4). Not all compounds analyzed were found in all soils: only fluoranthene and pyrene were present in all the soils studied, followed by benzo(*e*)pyrene, phenanthrene and chrysene that appeared in over 90% of the samples. Eight compounds (naphthalene, benzo(*a*)anthracene, benzo(*a*)pyrene, benzo(*k*)fluoranthene, indene, benzo(*g*,*h*,*i*)perylene, benzo(*b*)fluoranthene and benzo(*j*)fluoranthene) were found in 80–90% of the soils; acenaphthene, fluorene and anthracene happened in over 50% of the cases, whereas acenaphthylene was only found in 21% of the soils. Finally, dibenzo(*a*,*h*)anthracene was not detected in any sample. These detection frequencies are lower than those found, for example, in the city of New York, which reach 96–100% for all the compounds studied here (Azzolina et al., 2016), already suggesting a lower contamination status of Santiago in comparison to larger cities.

The sum of PAH concentrations in the surface soils ranged between 4 and 4728 ng g^{-1}, with a mean value of 508 ng g^{-1} (median 217 ng g^{-1}), whereas the sum of the 16 EPA PAHs ranged from 4 to 4216 ng g^{-1}, with a median of 193 ng g^{-1}. The concentrations found for the sum of PAHs are in the same ranges reported for other similar-sized cities with low population densities like Tarragona (42–1472 ng g^{-1}, Nadal et al., 2004), Viseu (6–790 ng g^{-1}, Cachada et al., 2012) or Ljubljana (218–4488 ng g^{-1}, Morillo et al., 2007). In turn, these values are much lower than in more populated cities like Krakow (Ciarkowska et al., 2019), New York (Azzolina et al., 2016), Lisbon (Cachada et al., 2012), Bratislava (Hiller et al., 2015), Tehran (Fazeli et al., 2019), Beijing or Shanghai (Li et al., 2018), which can reach concentrations typically 10

Table 3
Generic reference levels (ng g^{-1}) for 13 PAHs in soils, as established in the Spanish Law on contaminated soils (Ministry of Presidency, 2005). See Table 2 for abbreviations.

	Nap	Ace	Flu	Anc	Fla	Pyr	B(*a*)A	Chy	B(*b*)F	B(*k*)F	B(*a*)P	Ind	D(*a*,*h*)A
Industrial use	10	100	100	100	100	100	20	100	20	100	2	30	3
Urban use	8	60	50	100	80	60	2	100	2	20	0.2	3	0.3
Other uses	1	6	5	45	8	6	0.2	20	0.2	2	0.02	0.3	0.03
Number of soils over threshold	*0*	*0*	*0*	*0*	*0*	*0*	*2*	*0*	*0*	*0*	*21*	*0*	*0*

to 20 times higher than those found here. In this sense, Hindersmann et al. (2020) found in the Ruhr area (Germany), an important center of historic industrial activities including cities as Dortmund and Essen, much higher concentrations than ours in several orders of magnitude, with most of the soils having Σ16 EPA PAH concentrations within the range from 0.1 to 70 μg g^{-1}. Total amounts of PAHs in urban soils have been connected in the literature to both population density and industrial activities, with average content of PAHs in European soils of urban/industrial areas within the range of about 1000–3000 ng g^{-1} (Ciarkowska et al., 2019). In this sense, Santiago de Compostela has a low density of population of 438 inhabitants km^{-2}, and a low industry development with scarce historical industrial activities having taken place in the city, so limited sources of these compounds would be expected.

The study of depth distribution in soil 21 (Fig. 2, full results in Supplementary material, Table S5) showed that PAHs accumulate preferentially in the surface. Concentrations are very homogeneous in the upper 20 cm (around 2000 ng g^{-1} in total), and then quickly decrease down to very low values (under 200 ng g^{-1} at >40 cm). This is commonly observed because of the physicochemical properties of these molecules that confer them low mobility in soil, so they are typically limited to the surface, organic-rich horizons of soils in most cases (Wilcke, 2000).

Regarding individual PAH concentrations, fluoranthene and benzo(*e*)pyrene were the compounds found at the highest concentrations, followed by pyrene and chrysene, with median values over 20 ng g^{-1} and mean values around 60–70 ng g^{-1} in the four cases. Fluorene, acenaphthene and acenaphthylene were the compounds found in the lowest concentrations, in all cases with median values under 1 ng g^{-1}. All soils presented a very similar PAHs composition pattern, dominated by high-molecular weight molecules. In most cases, the distribution was approximately almost half 4 ring PAHs and half 5–6 rings PAHs, with small contribution from 2 to 3 ring compounds. This is a very similar pattern to reports in other cities (Ciarkowska et al., 2019; Fazeli et al., 2019; Gao et al., 2019), and different to what would be expected in non-polluted areas: a combination of low PAHs and dominance of 2–3 ring-

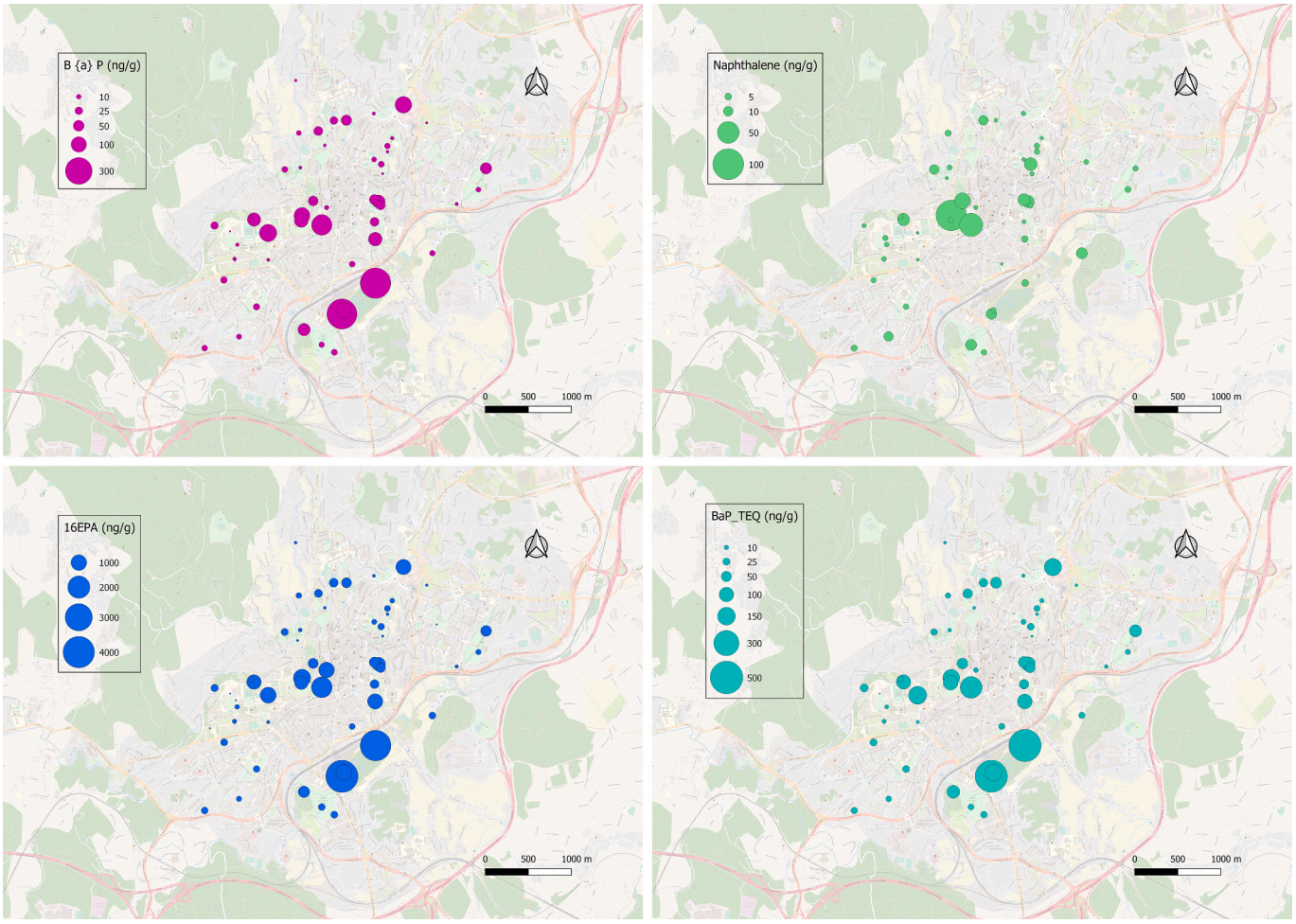

Fig. 3. Spatial distribution of PAHs in soils. Clockwise from upper left: benzo(*a*)pyrene; naphthalene; sum of 16 EPA PAHs; benzo(*a*)pyrene equivalent concentration.

Table 4
Pearson's correlation coefficients. See Table 2 for abbreviations. * significant at a *P*-value of 0.05; ** significant at a P-value of 0.01; *** significant at a P-value of 0.001.

	Nap	Acy	Ace	Flu	Phen	Anc	Fla	Pyr	B[*a*]A	Chy	B[*b*]F+B[*j*]F	B[*k*]F	B[*e*]P	B[*a*]P	Ind	B[*ghi*]P	∑PAHs	∑16EPA	BaPeq
Nap	1																		
Acy	0.004	1																	
Ace	0.66***	0.23	1																
Flu	0.64***	0.61***	0.83***	1															
Phen	0.46***	0.73***	0.73***	0.89***	1														
Anc	0.33*	0.88***	0.60***	0.85***	0.95***	1													
Fla	0.29*	0.86***	0.55***	0.80***	0.95***	0.98***	1												
Pyr	0.30*	0.86***	0.56***	0.79***	0.95***	0.98***	1.00***	1											
B[*a*]A	0.30*	0.84***	0.55***	0.79***	0.95***	0.97***	0.99***	0.99***	1										
Chy	0.22	0.80***	0.54***	0.71***	0.92***	0.94***	0.97***	0.97***	0.97***	1									
B[*b*]F + B[*j*]F	0.25	0.80***	0.51***	0.70***	0.91***	0.93***	0.98***	0.98***	0.98***	0.99***	1								
B[*k*]F	0.30*	0.81***	0.55***	0.76***	0.93***	0.94***	0.98***	0.98***	0.98***	0.98***	0.99***	1							
B[*e*]P	0.26	0.78***	0.55***	0.72***	0.92***	0.93***	0.98***	0.98***	0.98***	0.99***	1.00***	0.99***	1						
B[*a*]P	0.26	0.80***	0.55***	0.73***	0.93***	0.94***	0.98***	0.98***	0.98***	0.99***	0.99***	0.99***	0.97***	1					
Ind	0.25	0.81***	0.52***	0.72***	0.92***	0.94***	0.98***	0.98***	0.98***	0.99***	1.00***	0.99***	0.99***	0.99***	1				
B[*ghi*]P	0.27*	0.76***	0.53***	0.70***	0.91***	0.91***	0.96***	0.96***	0.96***	0.98***	0.99***	0.98***	0.99***	0.99***	0.99***	1			
∑PAHs	0.30*	0.82***	0.57***	0.77***	0.95***	0.96***	0.99***	0.99***	0.99***	0.99***	0.99***	0.99***	0.99***	1.00***	0.99***	0.98***	1		
16EPA	0.28*	0.83***	0.55***	0.75***	0.93***	0.95***	0.98***	0.98***	0.98***	0.98***	0.98***	0.98***	0.98***	0.98***	0.98***	0.97***	0.99***	1	
BaPeq	0.27*	0.81***	0.55***	0.74***	0.93***	0.94***	0.98***	0.99***	0.98***	0.99***	0.99***	0.99***	1.00***	1.00***	1.00***	0.99***	1.00***	0.98***	1
pH	0.19	0.17	−0.04	0.12	0.07	0.14	0.13	0.14	0.14	0.08	0.10	0.11	0.09	0.08	0.10	0.08	0.11	0.12	0.09
Clay	−0.14	0.02	−0.13	−0.10	−0.07	−0.06	−0.03	−0.04	−0.05	−0.005	0.02	0.01	−0.003	−0.01	0.02	0.02	−0.02	−0.01	−0.01
OC	0.17	−0.02	0.08	0.07	0.04	0.01	−0.01	−0.01	−0.03	−0.01	0.0001	0.02	-0.01	0.003	0.004	0.01	-0.0002	0.01	0.001
CIC	0.23	0.11	0.02	0.14	0.10	0.11	0.09	0.10	0.08	0.05	0.08	0.11	0.06	0.07	0.08	0.09	0.08	0.11	0.08
Pb	0.27*	0.18	0.47***	0.34*	0.49***	0.43**	0.50***	0.51***	0.53***	0.60***	0.60***	0.60***	0.60***	0.58***	0.60***	0.62***	0.56***	0.56***	0.58***
Cu	0.04	0.05	0.08	0.00	0.07	0.08	0.13	0.14	0.16	0.17	0.20	0.20	0.19	0.18	0.21	0.22	0.17	0.17	0.18
Zn	0.06	0.24	0.18	0.12	0.34*	0.35**	0.43**	0.44***	0.45***	0.55***	0.55***	0.52***	0.53***	0.51***	0.55***	0.55***	0.49***	0.49***	0.51***
Ni	−0.11	−0.01	−0,13	−0.14	−0.14	−0.10	−0.08	−0.08	−0.09	−0.06	−0.03	−0.07	−0.05	−0.06	−0.04	−0.03	−0.07	−0.06	−0.06
Cr	−0.06	−0.05	−0.06	0.10	0.14	−0.12	−0.11	−0.11	−0.12	−0.10	−0.09	−0.11	−0.10	−0.10	−0.10	−0.09	−0.11	−0.10	−0.11
As	−0.07	0.00	−0.04	−0.09	−0.07	−0.03	−0.04	−0.04	−0.04	−0.02	−0.05	−0.05	−0.04	−0.04	−0.04	−0.04	−0.04	−0.05	−0.06

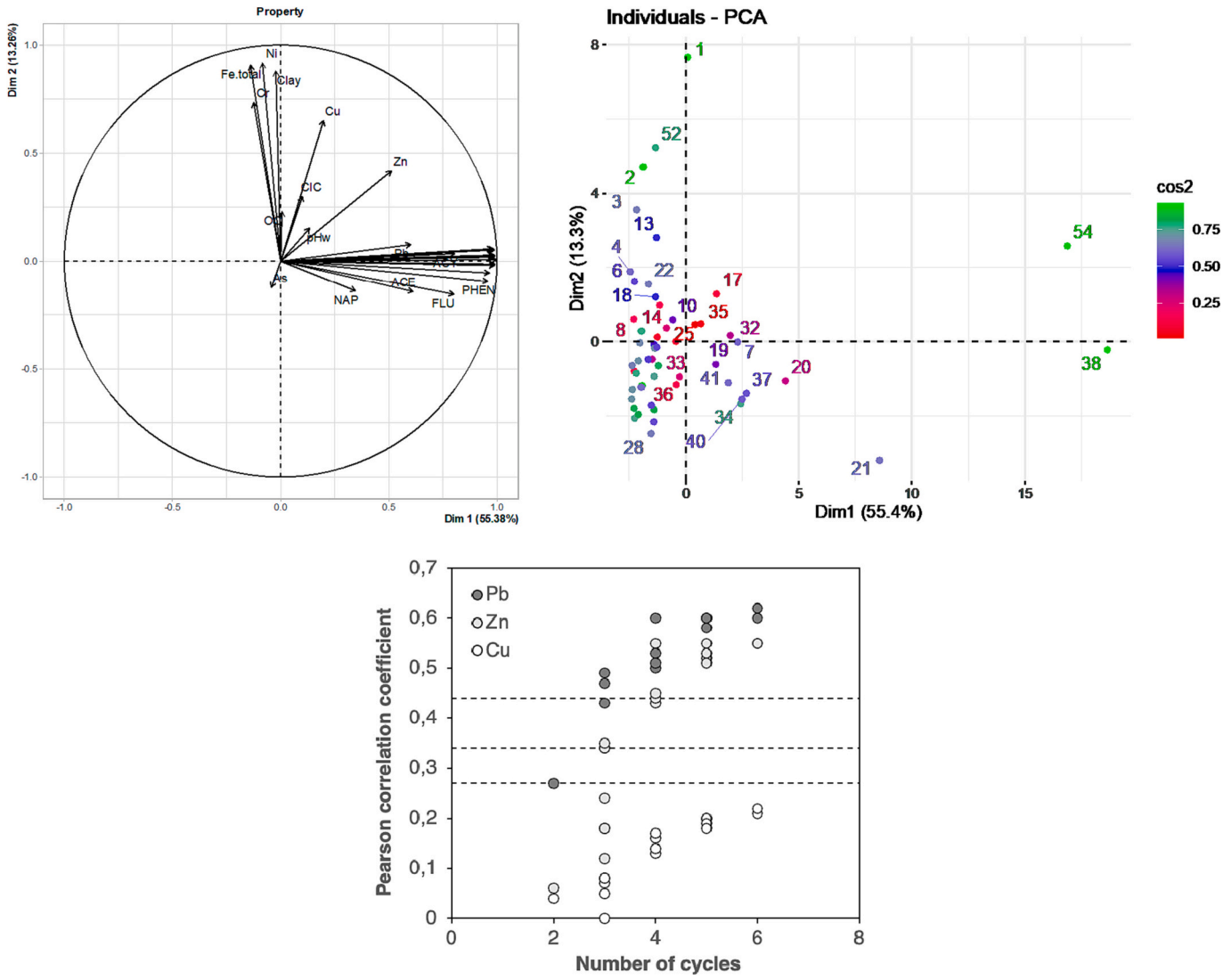

Fig. 4. Summary of PCA results and correlations of PAHs with trace elements.

molecules (Rate, 2022). Not surprisingly, all PAHs were strongly correlated among them with the exception of naphthalene (Table 4). Similar observations have been reported by Ciarkowska et al. (2019) in two Polish cities, where naphthalene did not correlate with the rest of PAHs. This suggests a different source for naphthalene than for the rest of compounds. The ratios B(*a*)A/Chy + B(*a*)A are over the value 0.35, what attributes PAH presence mainly to a combination of vehicle emission and coal combustion (Wang et al., 2013), and this will be in agreement with the strong correlation with Pb as we will see below. Besides, the ratios Fla./Fla. + Pyr and Ind/Ind + B(*ghi*)P over 0.5 in most soils indicate important contribution of coal combustion, whereas some soils presented values for both ratios in the range 0.4–0.5, what would mean a predominance of vehicle emissions in those cases (Rate, 2022). Overall, the results suggest that PAHs in this city are originated mainly from pyrogenic sources, both from coal and fuel combustion, as commonly found in other studies in urban soils (Li et al., 2018; Fazeli et al., 2019; Gao et al., 2019).

Comparison to soil protection levels confirms the low degree of pollution of the soils in relation to these compounds. The Spanish regulation on contaminated soils establishes generic reference levels (GRLs) for the protection of human health for the 14 PAHs indicated in Table 3. Soils would be considered contaminated when GRLs are surpassed by a factor of 100, what does not happen here in any case. For most PAHs studied, no soils were found over the "industrial use" GRL, and only two soils surpassed the GRL for "other uses" for B(*a*)A (soils 38 and 54), but not the GRL for urban use. Twenty-one soils surpassed the value established for "other uses" for B(*a*)P, of which two soils also surpass the value for urban use (soils 38 and 54 again).

On the other hand, the values for the B(*a*)P equivalent (BaPeq) range from 0.004 to 489 ng g^{-1}, with a median value of only 19.7 ng g^{-1}. This is indicative of a very low associated toxicity risk and no soil surpassed the value of 700 mg BaPeq kg^{-1}, established as a safe threshold by the Canadian Soil Quality Guidelines for the protection of environmental and human health (CCME, 2010). Also, in line with the low concentrations of individual PAHs found that we discussed above, the values for BaPeq in Santiago are similar to other small/medium cities like Viseu (Cachada et al., 2012) and lower than in larger cities like Lisbon (Cachada et al., 2012), Shanghai (Wang et al., 2013) or more industrialized ones (Cetin, 2016).

Spatial distribution shows similar patterns for all individual PAHs except naphthalene (Figs. 3 and S1). This different distribution pattern for naphthalene, in addition to the already mentioned lack of correlation with other PAHs, confirms the idea of a different origin/source for this compound. The rest of PAHs presented a comparable behavior in this sense, with overall similar spatial distribution patterns and the highest concentrations found in soils located in two areas: near to the oldest

historical park in the city center, and close to a highway in the southeast. Location has been signaled as a fundamental factor explaining PAH spatial distribution patterns in many works. Higher concentrations of PAHs often occur more along roadsides and industrial areas than in parks, commercial and residential districts (Li et al., 2018). However, in this case it is not clear why these two specific areas are enriched in PAHs. It is true that the soils with the highest PAH concentrations are located near high traffic intensity areas, but soils in other areas with high traffic intensity do not present similarly high PAH concentrations. Thus, the differences found are difficult to interpret in this case, what could be attributed to the typical human-driven spatial distribution of urban soils that results from modification by excavation, capping of imported soils or burying of old surfaces with fill and wastes (Rate, 2022).

Studies in the literature have commonly observed that differences in the distribution patterns of PAHs in urban soils can be controlled or influenced by factors other than location, such as vegetation cover or soil properties including soil organic matter content and soil microbial activity (Tang et al., 2005; Morillo et al., 2007; Peng et al., 2013; Li et al., 2018; Rate, 2022). However, in this case these relationships were not evident. Significant differences in PAHs concentrations due to land use were not observed (Table 2) and correlations of PAHs with soil physicochemical properties that could influence PAHs mobility, such as OM contents or clay content/texture, have not been observed either (Table 4). This suggests that PAH contents in these soils are not dependent on land use/vegetation or soil factors.

Yet, a relationship has been found between PAHs and inorganic pollutants, whose concentrations have been already reported (Herbón et al., 2021) and included here in correlation and PCA analyses, in order to investigate potential common sources of organic and inorganic pollutants. Significant positive correlations with PAHs were found for Pb and Zn (Table 4), worse for Zn than for Pb and also worse in the case of the lowest weight PAHs. The results of PCA analysis (Fig. 4) also suggest that Pb and PAHs have a common source, what seems logical, as they come mainly from combustion, and they show no relationship with edaphic properties. This is a typical behavior of soil pollutants from non-natural sources, in contrast to Ni or Cr, which are mainly of lithogenic origin in these soils (Herbón et al., 2021). Therefore, the results strongly suggest a common origin of PAHs and Pb, very likely traffic emissions that are a well-known major contributor to these compounds in urban soils (Wilcke, 2000).

4. Conclusions

The soils of the city of Santiago de Compostela present a low PAH pollution status compared to other cities, with lower concentrations and detection frequencies, in coherence with the low population density and low degree of industrialization of the city. Among the compounds considered, the higher risk is related to benzo(*a*)pyrene, whose concentrations surpassed the precautionary limits established in the Spanish Law in 21 out of the 55 soils. In any case, values are far from reaching the levels that would classify the soils as polluted. An important heterogeneity in spatial distribution of PAH concentrations was observed, with two specific areas within the city concentrating the highest PAHs contents. However, an influence of factors such as location in the city, soil properties or vegetation in the distribution of PAHs was not found. Overall, PAH concentrations are closely related to those of Pb, but not to other inorganic pollutants or edaphic properties, suggesting their main origin must be a common source, exogeneous and anthropic, likely a combination of combustion and traffic.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geodrs.2023.e00703.

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