Benzo[a]pyrene sourcing and abundance in a Coal Region in Transition reveals historical pollution, rendering soil screening levels impractical.

Carlos Boente (✉ carboente@gmail.com)

Universidad de Oviedo <https://orcid.org/0000-0001-8266-828X>

Diego Baragaño

Universidad de Oviedo

José Luis R. Gallego

Universidad de Oviedo

Research

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Abstract

Background

Benzo[a]pyrene (BaP) is a hazardous compound for human health and for environmental compartments. Its transfer and deposition through the atmosphere affects soil quality. In this regard, soil screening levels are commonly used to monitor the degree of soil contamination. However, these thresholds are often established without considering historical anthropogenic activities that affect soil (diffuse pollution). In this context, this study had the following objectives: 1) to identify the potential pollutant load of BaP, as well as other Polycyclic Aromatic Hydrocarbons (PAHs), in the soil of an area in a prominent Coal Region in Transition in NW Spain; 2) to test whether soil screening levels are realistic and whether they reflect the complexity of regions closely linked to heavy industries and mining; and 3) to determine whether there is a relationship between PAHs and inorganic pollutants.

Results

The 150 soil samples studied showed a notable content of high molecular weight PAHs. In this regard, BaP surpassed the threshold levels in practically the entire area. Samples fell into groups: a first group of outliers statistically determined through robust Mahalanobis distance, and three more by means of hierarchical cluster analysis. PAH-parent diagrams revealed a relatively homogenous fingerprint for all clusters. In addition, molecular diagnostic ratios pointed to coal combustion as the main pollution source, whereas only a few of the outliers appeared to be related to specific spills. The BaP background was calculated to be $0.24 \text{ mg} \cdot \text{kg}^{-1}$, exceeding the threshold limits established in Spain by more than 10 times. Finally, a factor analysis revealed a moderate correlation of BaP with elements usually associated with coal combustion, such as Tl and V.

Conclusions

The soils of regions associated with coal exploitation and heavy industry have an indelible pollution fingerprint, caused namely by BaP and other PAHs, which come to form part of the geochemical background. The use of official soil screening levels in such regions is therefore questionable, and hot points should be determined on the basis of soil backgrounds specifically calculated for these areas.

Background

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of Semi-Volatile Organic Compounds (SVOCs) found pervasively in various environmental compartments, such as soils, water, air and sediments [2, 13, 68]. In this regard, several studies have demonstrated that the number of humans exposed to PAHs through soils is higher than through air or water [45, 51, 73]. Given that these compounds are carcinogenic, mutagenic, teratogenic and toxic to all living organisms, there is a need to monitor their

concentration in soils [6, 56]. PAHs are listed as priority pollutants by the European Union and the United States Environmental Protection Agency [14, 20, 55], and they are becoming increasingly studied and tracked in soils worldwide [1, 11, 23, 64].

PAHs are often divided into 16 priority compounds. Among them, benzo[a]pyrene (BaP) is one of the most hazardous because of its carcinogenic and mutagenic properties and its persistence and bioaccumulation in the environment [66, 78]. Consequently, the European Union established in 2004 an atmospheric target value of 1 ng/m³ for BaP [18]. Regarding soils, Spanish legislation set out Risk-Based Soil Screening Levels (RBSSLs) for organic contaminants, based on toxicity parameters and land use. In this regard, these limits for BaP in soils are: 2 mg·kg⁻¹ for industrial use; 0.2 mg·kg⁻¹ for urban use; and 0.02 mg·kg⁻¹ for other uses (those that are neither urban nor industrial and that are suitable for agricultural, forestry and livestock-raising activities as defined in [62]).

PAHs can be natural or anthropogenic. Natural sources comprise incomplete natural combustion of carbon-containing fuel such as coal or wood (wildfires), or even volcanic eruptions and petroleum input in oil seeps [76]. On the other hand, energy production, industrial emissions, waste incineration, car exhausts, and biomass burning are common examples of anthropogenic sources [15, 74]. Another remarkable source of PAHs is coal mining since this activity involves the massive use of this fossil fuel for energy production in power stations and also coal waste accumulation and coal processing, which have also led to soil pollution by PAHs around the world [29, 30, 52].

Sources of PAHs can be studied using specific molecular ratios [33, 73]. In addition, multivariate statistical methods, such as hierarchical cluster analysis (HCA) and principal component analysis (PCA), can unravel relationships between inorganic and organic pollutants [47, 70]. Finally, geostatistical methods (e.g. kriging, inverse-distance weighting (IDW)) allow the characterization and evaluation of the geographical distribution of pollutants [8, 28, 40].

The municipality of Langreo (Asturias, NW Spain) is an area characterised by heavily industrialized mining activity. In this regard, multiple types of industries—some still in operation and others closed or abandoned—have released pollutants into the environment. By the mid XIX century, these industries had taken up coal mining as a primary activity. Since then, metallurgy, coal power stations, and chemical and fertilizer industries, among others, have successively occupied the main valley in the area [59]. Nowadays, the continuous transition towards cleaner energies and other technologies has impacted this area and many other similar regions in Europe [37], which have all experienced progressive abandonment that started with mine closures. In this context, the European Commission has recently drawn up a list of 14 Coal Regions in Transition, which includes Langreo. Along the same lines, in 2017, the European Commission launched a platform to encourage environmental studies of these areas, among other actions [3].

Potential soil pollution in the area of Langreo and also in specific brownfields has been previously addressed at various scales [9, 10, 22]. It has been concluded that soils of the zone present significant

pollution by Potentially Toxic Elements (PTEs), in particular As, Cu, Hg, Pb and Zn in Langreo itself [9] and the neighbouring area [26]. In this context, the simultaneous presence of PAHs and PTEs is foreseeable since both types of pollutant can be released by the same sources, as is the case of coal power stations releasing Cd, Cr, Pb, Tl, or V together with BaP and other PAHs [38, 61]. In this regard, soils, particularly in urban-peri-urban environments, can provide a geological record of multi point-source pollution [13, 75, 77].

Given the preceding considerations, this study had the following objectives: 1) to examine the presence of BaP and another 15 (EPA) priority PAHs in the soils of the municipality of Langreo (82 km²), located in the heart of a Coal Region in Transition; 2) to evaluate the validity of Spanish RBSSLs for BaP in the context of regions highly linked to coal mining and heavy industries; and 3) to ascertain whether there is a link between the PAH and PTE pollution observed in Langreo in previous studies. To this end, the study applied a methodology combining multivariate statistical and geostatistical approaches with molecular ratios. We propose that the strategy used herein can be easily extrapolated to studies of similar characteristics.

Methods

Study area and sampling strategy

The municipality of Langreo (Asturias, NW Spain, Fig. 1) is a traditional mining and industrial area whose origins date back to 1850. The most predominant activities have been coal mining, ferrous metallurgy, coal power stations and chemical industries [42]. This long and extensive activity has impacted environmental compartments, as evidenced in previous studies, e.g. PTEs in urban air [46], soils [10] and groundwater [7], and the presence of a number of abandoned brownfields in the area [22].

In the context of geomorphology, the Nalón river crosses this 82 km² municipality, which is comprised of a series of valleys with altitudes ranging from 200 to 900 m. Our sampling consisted of a representative set of data collected from grasslands, forests, and natural soils in rural and peri-urban areas. The sampling design followed a stratified systematic strategy, covering 10 equidistant transects (250 m wide and 1000 m apart) perpendicular to the Nalón river [9]. This specific direction was chosen to achieve representativeness of the hydrological sub-basins, which in this case are perpendicular to the river. Under this premise, 150 samples were gathered, with the number of samples per transect determined proportionally to its length, the location of sampling within the transects being random (Fig. 1).

Samples were taken from the first 20–25 cm of soil in each vertex of a 1-m square and its central point. After this, composite samples were passed through a 2-cm mesh screen to remove large material such as organic matter, rocks and gravel. They were then transported to laboratory, stored at 4°C to prevent biodegradation, and air-dried at room temperature to prevent evaporation.

Analytical procedures

Representative soil subsamples weighing 10 g were extracted with dichloromethane:acetone (1:1) in a Soxtherm system (Gerhardt). Concentrations of PAHs were then determined after sample injection into a 7890A GC System coupled to a 5975C Inert XL MSD with a Triple-Axis Detector (Agilent Technologies), following Environmental Protection Agency (EPA) method 8272 with modifications. A capillary column DB-5 ms (5% phenyl and 95% dimethylpolysiloxane) 30 m x 0.25 mm i.d. x 0.25 µm film (Agilent Technologies) was used, with He as carrier gas at a flow rate of 1 ml·min⁻¹. The initial oven temperature was 70°C (held for 2 min), and it was ramped up at 20 °C/min to 220 °C, raised to 270 °C at 10 °C/min (held for 1 min), then raised to 290 °C at 10 °C/min (held for 1 min), and finally ramped up at 10 °C/min to 300°C (held for 7 min). The gas chromatography (GC) injector was operated in splitless mode for 2 min, and its temperature was maintained at 260°C. The mass spectrometer was operated in selected ion monitoring mode (SIM), and the quantification m/z relations were as follows: 128 (Naphthalene, abbreviated N); 152, 153 and 154 (Acenaphthylene, Acy; and Acenaphthene, Ace); 165 and 166 (Fluorene, F); 178 (Phenanthrene, Phe; and Anthracene, Ant); 202 (Fluoranthene, Fluo; and Pyrene, Pyr); 228 (Benz[a]anthracene, BaA; and Chrysene, Chr); 252 (Benzo[b]fluoranthene, BbF; Benzo[k]fluoranthene, BkF; and Benzo[a]pyrene, BaP); and 276 and 278 (Dibenz[a,h]anthracene, DbA; Benzo[ghi]perylene, BghiP; and Indene[1,2,3-cd]pyrene, Ind). The mass spectrometer was operated in electron ionization mode (EI) at 70 eV and was calibrated daily by auto-tuning with perfluorotributylamine (PFTBA). In addition, a qualitative full-scan analysis with a mass range acquisition from 45 to 500 (m/z) was also performed in relevant samples (see results).

In addition, the PTE content of the 150 samples was taken from a geochemical database reported in a previous study [9]. In brief, measurements were carried out by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) after 1:1:1 “aqua regia” digestion (ISO 9002-accredited Bureau Veritas Laboratories, Vancouver, Canada). The elements analysed and detection limits were: As (0.1 ppm); Ba (0.5 ppm); Cd (0.01 ppm); Co (0.1 ppm); Cr (0.5 ppm) Cu (0.01 ppm); Hg (5 ppb); Mo (0.01 ppm); Ni (0.1 ppm); Pb (0.01 ppm); Sb (0.02 ppm); Tl (0.02 ppm); V (2 ppm); and Zn (0.1 ppm).

Outlier identification and clustering

Correct application of the multi-variate statistics requires previous detection of extreme values representing anomalous data. Therefore, outliers were identified by means of the percentile 95 of the robust Mahalanobis distance, which is an accepted method to identify anomalous data [44]. The general expression is defined by Eq. (1) as

$$d(\text{Mahalanobis}) = [(X_b - X_a)^T \cdot C^{-1} \cdot (X_b - X_a)]^{0.5} \quad (1)$$

where Xa and Xb are the pair of objects and C is the sample covariance matrix. All samples identified as outliers through this equation were included in Cluster 1 (see below).

The remaining samples were grouped in terms of a HCA (Hierarchical Clustering Analysis) that was carried out using SPSS v. 24 software by means of the Ward algorithm and Euclidean distance [50].

Molecular ratios

PAHs were divided into two main groups of compounds on the basis of the number of aromatic rings; low molecular weight PAHs (LMW PAHs, 2–3 aromatic rings) and high molecular weight PAHs (HMW PAHs, 4 or more aromatic rings). HMW PAHs are produced mainly by pyrogenic processes while LMW PAHs have both petrogenic and pyrolytic sources. Thus, a concentration ratio of HMW/LMW > 1 may reflect the pyrogenic nature of PAHs [71]. In subsequent steps, a large number of molecular ratios can be calculated conceived, and some such ratios were used in this study to propose sources (Table 1).

Table 1. List of typical PAH ratios and molecular indices used in this study for source diagnosis, together with their typical reported values.

Ratio	Range/value	Source	Reference
$\Sigma\text{HMW}/\Sigma\text{LMW}$	> 1	Pyrogenic	[80]
	< 1	Petrogenic	
Fluo/(Fluo+Pyr)	< 0.4	Petrogenic	[17]
	0.4 - 0.5	Fuel combustion	
	> 0.5	Grass, wood and coal combustion	
Ind/(Ind + BghiP)	< 0.2	Petrogenic	[79]
	0.2 - 0.5	Fuel combustion	
	> 0.5	Grass, wood and coal combustion	
A/(A+Phe)	< 0.1	Petrogenic	[58]
	> 0.1	Pyrogenic	

As seen above, ratios such as Fluo/(Fluo + Pyr) and Ind/(Ind + BghiP) provide a larger discrimination within pyrogenic sources, whereas others such as A/(A + Phe) are applied specifically to differentiate between petrogenic and pyrogenic sources.

Spatial distribution of Benzo[a]pyrene

The spatial distribution of a variable can be determined through geostatistical techniques. Of these, Ordinary Kriging (OK) is a widely accepted interpolation approach used in environmental studies when data present a Gaussian distribution. In this regard, the performance of an interpolation by OK requires the design of a variogram, that is used to calculate the spatial variation structure of regionalized variables [27, 31]. It is defined as follows (Eq. 2)

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (2)$$

where h is the distance argument, and Z(Xi) and Z(Xi + h) are numerical values of a variable observed at point Xi and Xi + h. N(h) is the number of pairs forming for an h distance. Therefore, it is the median value

of the square of the distances between all pairs of points in the geometric field spaced at an h distance [43].

In this study, OK was used to determine the spatial distribution of BaP in the soils of Langreo. Given the known presence of outliers, normality conditions could not be achieved with raw data and thus a log-transformation was used. The geostatistical simulation was done using Biomedware's SpaceStat v. 4.0 software.

Correlation Benzo[a]pyrene - PTEs

The degree of relationship between BaP and PTEs was studied by factor analysis. The number of factors was determined by the Kaiser/Guttman criterion while the principal components method was used for factor extraction, following recommendations for geochemical data [21, 63]. These calculations were made using SPSS v. 24.

Results And Discussion

PAH content in the study area

The descriptive statistics for PAH concentrations of the 150 soil samples in Langreo are shown in Table 2. At first glance, a notable variability in the concentrations of all the compounds can be appreciated. This observation implies marked heterogeneity in these soils in terms of PAH content, especially those with four or more rings (HMW PAHs), as suggested by many high RSD values, which are concordant with the differences between the mean and the median. On the whole, data did not show normality, thus evidencing the presence of outliers.

In turn, our results also revealed the predominance of HMW PAHs. If we apply the most restrictive Spanish RBSSLs, namely "other uses" (in fact this category accounts for more than 90% of the soils where the samples were taken), around 5–15% of samples exceeded the threshold levels for heavy PAHs such as BaA, BbF, DbA and Ind. Of note, BaP surpassed the legal limits in 79% of the samples, presenting a median that was almost 20 times the value of the RBSSL.

Table 2. Statistical summary of the analysis PAHs in the 150 samples. Range, Mean and Median and relative standard deviation (RSD). The RSD after outlier removal (RSD*, see above) and the most restrictive RBSSL are also provided. All units are expressed in $\text{mg}\cdot\text{kg}^{-1}$, except RSD and RSD*, which are expressed as a %.

PAH	Rings	RBSSL	Range	Mean	Median	RSD	RSD*	No. Samples surpassing RBSSL
N	2	1	0.01-0.74	0.06	0.02	182	172	0
Acy	3	-	0.01-0.36	0.03	0.01	190	111	-
Ace	3	6	0.01-3.1	0.04	0.01	710	52	0
F	3	5	0.01-2.6	0.03	0.01	612	80	0
Phe	3	-	0.012-70	0.64	0.06	898	123	-
A	3	45	0.01-13	0.13	0.01	836	115	0
ΣLMW	-	-	0.062-89.4	0.92	0.13	795	110	-
Fluo	4	8	0.01-140	1.18	0.09	970	125	1 (0.7%)
Pyr	4	6	0.01-120	1.00	0.07	982	124	1 (0.7%)
BaA	4	0,2	0.01-50	0.44	0.04	928	121	17 (11%)
Chr	4	20	0.01-48	0.45	0.06	868	115	1 (0.7%)
BbF	5	0.2	0.01-68	0.64	0.07	874	123	33 (22%)
BkF	5	2	0.01-21	0.20	0.02	847	123	1 (0.7%)
BaP	5	0.02	0.01-42	0.38	0.04	895	129	119 (79%)
DbA	5	0.03	0.01-5.7	0.06	0.01	778	93	17 (11%)
BghiP	6	-	0.01-35	0.32	0.04	893	118	-
Ind	6	0.3	0.01-2.3	0.09	0.04	239	124	8 (5%)
ΣHMW	-	-	0.1-530	4.75	0.46	910	120	-
ΣPAH	-	-	0.163-619	5.67	0.62	891	111	-

Outliers and clustering

The high RSDs suggest the presence of outliers in the data set. To identify these outliers, percentile 95 of the Robust Mahalanobis distance was used. The results are shown in Fig. 2. Seven samples were identified as outliers and separated into an independent group (namely Cluster 1). Once outliers had been identified, the statistical analysis was repeated with the remaining 143 samples. An improvement in normality was observed, mainly through the reduction of the RSD coefficient (see RSD*, in Table 2).

The exclusion of outliers is also useful to reduce uncertainty and noise, thereby enhancing group formation in the HCA. In this context, the dendrogram resulting from this multivariate analysis of PAHs in the 143 soil samples was mapped as shown in Fig. 3, together with the mean content of LMW, HMW PAHs and also BaP. Three clusters (four after manual addition of Cluster 1 - Outliers) were found.

- Cluster 1: Corresponding to the 7 outliers previously identified. The concentrations of LMW and HMW PAHs were very high in these samples with regard to the other groups, and therefore mean values should be interpreted with care due to the presence of extreme values.
- Cluster 2: This was the group with the lowest number of samples (5), all of them located in the urban/peri-urban area of Langreo. These samples presented a notable concentration of HMW PAHs. Given the size of the group and values, this group could be considered an extension of Cluster 1.

- Cluster 3: This group (35 samples) comprised soils with a moderate concentration of HMW PAHs. The samples were generally located halfway between peri-urban and rural areas, further away from urban cores or heavy industries than Clusters 1 and 2.
- Cluster 4: This group (103 samples) was the most numerous and included samples with lower PAH concentrations than the previous clusters. It showed the same pattern of decreasing concentrations with increasing distance from the urban-industrial core (Fig. 3). Note that this cluster contained samples that did not surpass the RBSSL for BaP and also some that surpassed this value slightly. Consequently, this group corresponded to soils with a lower degree of contamination.

On the whole, the concentration of PAHs in the soil increased dramatically with proximity to the urban and industrial core (Fig. 3). The pollution was, therefore, located mainly in areas that held the the largest number of sources.

PAH sources

Of note, the distribution of individual PAHs revealed a relatively homogeneous fingerprint for the four clusters (predominance of 3-4-ring compounds such as Phenanthrene, Fluoranthene and Pyrene), thereby suggesting similar profiles and common sources (Fig. 4), with the possible exception of Cluster 1.

Regarding the molecular diagnostic ratios, the mean concentration ratio of $\Sigma\text{HMW}/\Sigma\text{LMW}$ was higher than 1 for all the clusters, initially suggesting that the PAH source was pyrogenic (Table 3)[80]. Furthermore, the $A/(A + \text{Phe})$ ratio reaffirmed the pyrogenic hypothesis, as values higher than 0.1 were found [58]. The values found for the $\text{Ind}/(\text{Ind} + \text{BghiP})$ and $\text{Fluo}/(\text{Fluo} + \text{Pyr})$ ratios suggest grass, wood and coal combustion [17, 79]. According to these data and the industrial profile of the area, coal burning activities (power station, metallurgical activities, chemical industry, etc.) are most likely to be the main source of PAHs. However, emission from the coal-fuelled heating systems in houses cannot be ruled out as these systems were used for decades (still active in many locations) both in rural and urban areas.

Table 3. Molecular diagnostic ratios for mean concentrations of PAHs for each cluster.

Cluster	$\Sigma\text{HMW}/\Sigma\text{LMW}$	$A/(A+\text{Phe})$	$\text{Ind}/(\text{Ind}+\text{BghiP})$	$\text{Fluo}/(\text{Fluo}+\text{Pyr})$
1	5.72	0.17	0.50	0.54
2	5.95	0.23	0.50	0.55
3	3.14	0.15	0.50	0.55
4	3.20	0.19	0.50	0.55

Nevertheless, it should be noted that these and other ratios have several limitations [71]. In fact, relative proportions of the organic compounds are usually assumed to be conserved between each emission source and the downwind measurement point [65], and they do not take into account possible alterations of the target compounds in soil (biodegradation, etc.). This implies that the diagnostic ratio results

should preferably be used as a guiding methodology to reinforce a hypothesis and not as a conclusive tool. In this context, here we applied the molecular diagnostic ratios combined with complementary interpretation methods, such as the cluster analysis and the factor analysis (see below).

On the other hand, the previous statement (diffuse pollution caused by pyrogenic PAH sources) could be masking the additional existence of potential point-sources. In this context, although the identification of local point sources (associated with brownfields, spills, waste disposal, etc.) was beyond the objectives of this work, the two main outliers found (samples 76 and 29 as shown in Fig. 2) were analysed in-depth to exemplify the superposition of diffuse and point source effect., this was done using a qualitative GC-MS approach. As shown in Fig. 5a, the chromatographic fingerprint of sample 76 differed greatly to that of 29. Indeed, the former reflects the fingerprint of a coal tar distillate [19] while the latter shows a typical profile of an oil derivative [36]. However, at the same time, the star diagram revealed a very similar PAH fingerprint profile for both samples (Fig. 5a). For sample 76, additional information from specific compounds such as alkanes (Fig. 5b) revealed the abundance of odd carbon number n-alkanes, typical of terrestrial vegetation [57; 72], whereas the alkane fingerprint of sample 29 showed the abundance of light-medium n-alkanes and isoprenoids, as corresponds to petroleum products [57]. Finally, detailed insight into a representative PAH (phenanthrene, see Fig. 5c) showed a clear predominance of the parent-PAH in sample 76, thereby pointing to the coal tar hypothesis [67]. In contrast, the PAH alkyl-derivatives in sample 29 were much more abundant, suggesting a mixture of both pyrogenic and petrogenic inputs [79].

Benzo[a]pyrene: A real anomaly in the study area?

A geostatistical analysis of BaP content was carried out to determine its distribution across the study area. OK was applied after performing a log-transformation of the 150 data set of BaP analyses in order to improve normality conditions, which are mandatory in kriging. The resulting map is shown in Fig. 6a. As with PAHs, the concentration of BaP in soils was higher in the urban and peri-urban area than in the rural environments. In addition, the predicted content consistently surpassed the RBSSL ($0.02 \text{ mg}\cdot\text{kg}^{-1}$). This observation reflects the high degree of pollution present in the soils. In this respect, from the regulatory perspective, practically any site within the entire municipality would require site-specific risk assessment to determine contamination by BaP. Consequently, it is questionable whether the official RBSSLs in Spain are useful in areas with a long history of industrial activity, particularly in Coal Regions in Transition.

Moreover, as seen in the map, BaP enrichment in soils presents a trend towards the full range of NW/SE directions (see 3D images in Fig. 6b). According to data from MERRA-2 (Modern-Era Retrospective Analysis from NASA, see [24], wind direction in Langreo is preferentially westerly from mid-February to the end of April; northerly, from May to mid-September; and southerly from mid-September to mid-February, while easterly winds are never predominant in this area. These wind patterns are consistent with the abovementioned spatial distribution of BaP—which is also conditioned by the topography—thereby

strongly supporting the notion that PAH diffusion occurs by atmospheric deposition through the main valley.

Given the preceding considerations, we conclude that the soil background of the municipality of Langreo present a high enrichment in BaP. An indicative value can be calculated by the method previously used in [10 and references therein] for trace elements in Langreo. In brief, and once excluding the samples in Cluster 1 (outliers), the geochemical background (threshold) can be calculated in a straightforward manner through the mean BaP concentration plus two times the standard deviation of the data set. Following this procedure, the resulting background concentration was $0.24 \text{ mg}\cdot\text{kg}^{-1}$, more than ten times the RBSSL for “other uses” of soil ($0.02 \text{ mg}\cdot\text{kg}^{-1}$), and even above the RBSSL for urban uses ($0.2 \text{ mg}\cdot\text{kg}^{-1}$). The background obtained was in the same range as other locations with BaP-enriched soil, such as the areas of Abadan, Iran ($0.061 \text{ mg}\cdot\text{kg}^{-1}$) [25], Sydney, Australia ($0.22 \text{ mg}\cdot\text{kg}^{-1}$) [54], Delmarva, USA ($0.39 \text{ mg}\cdot\text{kg}^{-1}$) [35], Berre, France ($0.26 \text{ mg}\cdot\text{kg}^{-1}$) [4], Mecocacán, Mexico ($0.22 \text{ mg}\cdot\text{kg}^{-1}$) [5], and Torino, Italy ($0.23 \text{ mg}\cdot\text{kg}^{-1}$) [49].

In conclusion, the soils of Langreo, an area with a long history of industrial activity, present a geochemical background that is highly enriched in BaP, surpassing the Spanish RBSSL. This finding can be explained by the fact that the RBSSLs for PAHs are based on toxicological values and do not consider historical backgrounds. The legislation of other countries has less restrictive limits for BaP in soils (Table 4). However, the background of Langreo would even surpass many of these limits. The wide range of toxicological data and methodologies used to establish such limits do not consider the effects of historical diffuse pollution. Consequently, these levels do not have the precision needed to evaluate BaP pollution in heavily industrialized areas, such as the one presented here or other sites with similar characteristics worldwide.

Table 4. Comparison of the Langreo background and RBSSLs in Spain and other countries.

Location	BaP $\text{mg}\cdot\text{kg}^{-1}$	Restriction	Reference
Langreo background	0.24	-	This study
Spain	0.02 / 0.2	Other / residential use of soil	[62]
United Kingdom	0.15	Land recovery threshold	[41]
Czech Republic	0.1	General soil screening value for negligible risk	[69]
Netherlands	0.26	Maximum permissible concentration in soils	[32]
Slovakia	0.1	General soil screening value for negligible risk	[69]
Denmark	0.1	Very sensitive land use	[16]
New Zealand	0.27	Residential soil use (surface < 1 m)	[48]

BaP correlation with PTE anomalies

A previous study reported the presence of PTE anomalies in the soil of Langreo [9]. Therefore, there may be a relationship between pollution by PTEs and PAHs, since the industrial processes described in previous sections facilitate the co-occurrence of both inorganic and organic contaminant emission. To this end, we carried out factor analyses, considering the multivariate database, including PTEs [9], together with the new BaP data. In order to identify different trends, we applied two approaches with enough samples to offer statistical significance. The first used the 47 samples from Clusters 1, 2 and 3 (corresponding to the soil with the highest PAH concentrations, as shown above), while the second used the 103 samples of Cluster 4, with the lowest concentrations. The results are shown in Table 5.

For the first case, the value of the Kaiser-Meyer-Olkin test for the factor analysis was a significant 0.782, providing reliable results. Three factors explained more that 80% of the total variance:

- The first factor comprised Cu, Pb, Cd, Sb, Zn, Ba and Cr, a typical association of heavy metals that contains some of the main pollutants of the area [9]. BaP showed a null relationship with this group, suggesting that the sources differed. In this regard, previous studies reported the presence of some of these potential pollutants linked to the heavy industry (metallurgy mainly) and traffic, especially Pb [39, 60].
- The second factor included high loads for V, As, Tl, and secondarily for Mo and Fe, together with the highest load of BaP (0.631). V and Tl are frequently associated with coal emissions [12, 38], and in Langreo they have been previously linked to coal combustion and are therefore detected in PM₁₀ particles [53]. Moreover, As has also been identified as a common pollutant in activities involving coal burning [34]. This association with typical trace elements of coal emission supports the hypothesis of the sources of PAHs presented above. However, BaP presented a low communality (0.415), which suggests that it shows a distinct behaviour to that of these elements.
- Co, Mn, Ni and Mg were included mainly in a third group. This association probably corresponds to geogenic elements present in background concentrations in the area.

The results for the “low pollution” Cluster 4 (KMO = 0.702) demonstrated BaP loadings (Table 5) divided among three distinct factors without special significance, and no clear relationship with any inorganic element. This finding suggests that the lower extent of pollution in rural areas dilutes the correlation between organic and inorganic emissions.

Table 5. Factor loadings, percentage of variance explained by the Varimax-rotated factors (extracted by principal components) and communalities. Highest loadings for factor are marked in bold. Pearson’s Coefficient with BaP is also included.

Cluster 1+2+3 (Higher pollution)					Cluster 4 (Lower pollution)					
	F1	F2	F3	Com.		F1	F2	F3	F4	Com.
Cd	0.982	0.086	0.126	0.988	Co	0.910	0.044	-0.003	0.015	0.831
Sb	0.981	0.086	0.110	0.982	Ni	0.852	0.137	0.087	-0.167	0.823
Cu	0.980	0.090	0.141	0.988	Mn	0.744	0.076	-0.013	-0.050	0.562
Pb	0.975	0.142	0.113	0.983	Cu	0.680	0.432	-0.163	0.356	0.804
Zn	0.956	0.168	0.193	0.979	Fe	0.658	-0.038	0.598	-0.089	0.808
Ba	0.870	0.147	0.292	0.863	Mg	0.568	0.069	0.074	-0.426	0.665
Cr	0.740	0.289	0.366	0.765	Pb	-0.020	0.904	0.042	0.096	0.828
V	0.061	0.849	-0.191	0.761	Ba	0.224	0.853	0.027	-0.097	0.788
As	0.357	0.778	0.060	0.737	Zn	0.445	0.767	0.147	0.148	0.841
Tl	0.177	0.748	-0.272	0.664	BaP	-0.092	0.377	0.323	0.274	0.340
Mo	0.586	0.693	-0.009	0.824	V	-0.023	-0.065	0.794	0.417	0.826
Fe	0.235	0.677	0.530	0.794	Cr	0.420	0.321	0.728	-0.200	0.860
BaP	-0.080	0.631	0.105	0.415	Tl	-0.264	0.142	0.567	0.129	0.600
Co	0.278	-0.062	0.903	0.896	As	-0.076	-0.066	0.188	0.792	0.674
Mn	-0.005	0.118	0.820	0.686	Sb	-0.063	0.495	-0.250	0.663	0.813
Ni	0.430	0.014	0.816	0.851	Mo	0.037	0.470	0.272	0.586	0.639
Mg	0.178	-0.311	0.770	0.721	Cd	0.181	-0.014	-0.018	0.032	0.763
Cumul. expl. var. (%)	49.575	69.299	81.759		Cumul. expl. var. (%)	29.143	47.706	59.365	66.793	

Conclusions

Here we conducted a high-density soil sampling and analysis (150 samples) in one of the historically most industrialized areas of Spain. Our results revealed high HMW PAH concentrations for BaA, BbF, DbA, Ind, and a particularly anomalous content of BaP.

Multivariate statistics were used to group samples within the study area after the identification of outliers via the Mahalanobis distance. We conclude that clustering is influenced mainly by the total concentration of PAHs, which is lower in soils of the rural or mountainous areas than in the urban and peri-urban zones. Most of the anomalous PAH contents were attributed to atmospheric deposition of pyrogenic particles originated in coal combustion processes, as revealed by molecular diagnostic ratios (diffuse pollution). However, some of the outliers found had local point-source origins, which should be addressed in further studies given the very high concentrations detected. The location of the main industries and the urban core, the predominant winds, and the topography of the area emerge as key factors in the distribution of the pollutants. Also, BaP showed a partial but significant correlation with PTEs commonly associated with coal combustion, such as V, Tl and As. This observation thus supports the hypothesis of pollution by atmospheric deposition.

Regarding the BaP anomaly, our geostatistical study confirmed that its concentration greatly exceeds the RBSSLs in the entire study area. In this context, a geochemical background of $0.24 \text{ mg}\cdot\text{kg}^{-1}$ was found,

surpassing the Spanish RBSSLs currently in force (based on only toxicity features and soil use). Consequently, this study questions the usefulness of RBSSLs as a valid reference for areas with a high density of heavy industries (past and present), particularly those linked to coal. This consideration should be taken into account when developing environmental policies for Coal Regions in Transition.

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Abbreviations

Ace: acenaphthene; **Acy**: acenaphthylene; **Ant**: anthracene; **BaA**: benz[a]anthracene; **BaP**: benzo[a]pyrene; **BbF**: benzo[b]fluoranthene; **BghiP**: benzo[ghi]perylene; **BkF**: benzo[k]fluoranthene; **Chr**: chrysene; **DbA**: dibenz[a,h]anthracene; **EC**: European Commission; **El**: electron ionization; **EPA**: Environmental Protection Agency; **EU**: European Union; **F**: fluorene; **Fluo**: fluoranthene; **GC**: gas chromatography; **HCA**: hierarchical cluster analysis; **HMW**: high molecular weight; **ICP-MS**: inductively coupled plasma mass spectrometry; **IDW**: inverse-distance weighing; **Ind**: indeno[1,2,3-cd]pyrene; **INDUROT**: Institute of Natural Resources and Territorial Planning (University of Oviedo); **kg**: kilogram; **LMW**: low molecular weight; **mg**: milligram; **N**: naphthalene; **NASA**: National Aeronautics and Space Administration; **NW**: Northwest; **OK**: Ordinary Kriging; **PAH**: Polycyclic Aromatic Hydrocarbon; **PCA**: principal component analysis; **PFTBA**: perfluorotributylamine; **Phe**: phenanthrene; **PTE**: Potentially Toxic Element; **Pyr**: pyrene; **RBSSL**: Risk-

Based Soil Screening Level; **RD**: Real Decreto (A decree made by the Spanish Government); **RSD**: relative standard deviation; **SE**: Southeast; **SIM**: selected ion monitoring

Declarations

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Authors' contributions

C. Boente and D. Baragaño were responsible for the sampling campaign, and preparation and analysis of samples. C. Boente led the writing and composition of tables/figures and structured the article. D. Baragaño provided support for the writing and a second opinion regarding the discussion and conclusions. J.R. Gallego coordinated the work, participated in the design of the experimental section, the interpretation and discussion of results, and supervised the manuscript.

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Availability of data and materials

The dataset used and/or analysed in this study is available from the corresponding author upon reasonable request.

Ethics approval and consent to participate

Not applicable.

Consent for publication

All authors read and provided their consent for publication.

Competing interests

The authors declare that they have no competing interests.

Author details

¹ *INDUROT and Environmental Technology, Biotechnology and Geochemistry Group, Campus de Mieres, Universidad de Oviedo, 33600, Mieres, Spain*

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Figures

Figure 1

Location of the study area in Spain and sampling design.

Figure 2

Robust Mahalanobis distance for the PAH data matrix of the Langreo soils. The horizontal line corresponds to the cut-off value equal to percentile 95 of the Mahalanobis distance. Samples over the line were considered outliers.

Figure 3

Graphical clustering and mean concentration of LMW and HMW PAHs and BaP for each cluster.

Figure 4

Parent-PAH distribution (% normalized) for the mean concentration of individual PAHs in the four clusters obtained after outlier detection and HCA.

Figure 5

a) Total Ion Chromatograms (TIC) of two outliers, the first one (top) showing a typical fingerprint of a coal-tar derivative (PAHs predominant), and the second (bottom) a petroleum product (lubricant oil, fuel oil or similar with n-alkanes predominant). The PAH star diagram (right) does not reflect many differences between the samples. (b) Single Ion Monitoring (SIM) chromatogram (m/z 57) of the same samples revealing only some high-molecular weight odd numbered n-alkanes in the first case and a complete series of n-alkanes and isoprenoids in the second. (c) Merged SIM (m/z = 178, 192 and 206 respectively) chromatograms for phenanthrene and alkyl derivatives (both C₁- and C₂-) (m/z = 178, 192 and 206 respectively), note the predominance of the parent PAH over the substituted compounds (top) and the inverse situation (bottom). Phe: Phenanthrene; A: Anthracene; Fluo: Fluoroanthrene; Pyr: Pyrene; BaA: Benzoanthracene; Chr: Chrysene; BghiP: Benzoperylene; Pr, pristane; Ph, phytane; nCn: n-alkanes; C₁-Phe: Methyl phenanthrenes; C₂-Phe: Dimethyl phenanthrenes.

Figure 6

a) Ordinary kriging (OK) results and experimental variograms for BaP concentration in soils. Shaded areas correspond to the city. b) 3D representation over Digital Terrain Model (DTM).