



## PAHs and trace metals in marine surficial sediments from the Porcupine Bank (NE Atlantic): A contribution to establishing background concentrations



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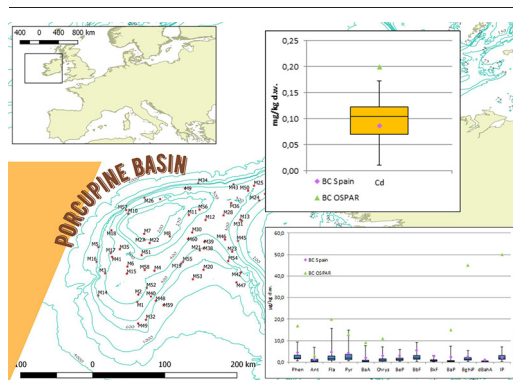
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### HIGHLIGHTS

- Spatial evaluation of the presence of a range of PAHs and trace metals in the Porcupine Basin
- Derivation of background values of PAHs and metal(loid)s suitable for the North Atlantic region
- Comparison with other background values with other Atlantic areas
- The data generated and the expansive off-shore area sampled can support MSFD GES assessment.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Little is known about pollutant concentrations in marine remote areas such as the Porcupine Bank in the NE Atlantic Ocean. Remote locations are much less studied than the more readily accessible coastal areas, nevertheless, are of great importance both to unveil how far human influence has reached and, are more challenging, to infer background concentrations (BCs) of naturally occurring and/or anthropogenic pollutants. Knowledge of contaminant background levels are critical for establishing remediation and management strategies; in addition, background assessment is heavily emphasised in legislative monitoring requirements. Obtaining suitable sampling locations to assess background concentrations can be challenging, as samples should match characteristics to the target area and not be impacted by historical or current inputs of the chemical substances of study. Anthropogenic impacts generally deem local-based sampling to be unsuitable to infer background pollution values. Sampling in remote areas such as the Porcupine Bank better fulfils low impact and pressure requirements making them more suitable for the derivation of background concentration estimates for organic compounds and metals.

The total concentrations of polycyclic aromatic hydrocarbons (PAHs) and metal(loid)s in deep sea sediments were evaluated and both an environmental status and a set of concentration data were adequate to derive BCs concentrations is presented. Concentration data indicated, in comparison with previous published data, trace level presence of PAHs and metal(loid)s in sediments from the Porcupine Bank. These values will provide a valuable tool to identify the natural presence of organic and inorganic compounds and be the basis to perform a sound environmental assessment.

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## 1. Introduction

The Porcupine Bank is located in the North-Eastern Atlantic, ~200 km off the west coast of Ireland, forming a seamount-like structure. The north-western part is limited by cliffs whereas in the eastern part the bank is connected to the Irish shelf by the narrow Slyne Ridge. The Porcupine Bank location is important from a fishery perspective (Bañón et al., 2020; Fernández-Zapico et al., 2013; Johnston et al., 2010; Ordines et al., 2017; O'Riordan, 1984; Ruiz-Pico et al., 2018), its potential natural resource reserves (Levell et al., 2010; Mann et al., 2003) and also for the presence in the upper canyon of cold-water corals forming reefs and mounds up to 30 m tall and 28 km long (Lim et al., 2020). Despite the recognized importance of the area, in terms of fishery and mining opportunities, it has been scarcely studied in respect of contaminants presence. This lack of information is mainly due to two reasons: there is generally more interest in coastal areas and it is harder to work in deep waters.

The measurement of PAHs and inorganic compounds (referred to as trace metals for simplicity, as the term metal is used without distinction between the target metals and metalloid (As)), is often used to evaluate the environmental status of an area. PAHs are a large group of organic compounds with two or more fused aromatic rings; while PAHs can naturally occur their presence in marine sediments is largely a result of anthropogenic emissions (such as fossil fuel-burning, motor vehicles, waste incineration, oil refining, oil spills). PAHs have received increased attention because of their potential carcinogenicity, mutagenicity and teratogenicity to aquatic organisms (CCME (Canadian Council of Ministers of the Environment), 2008). European Directives such as WFD (Water Framework Directive) regulate the presence of these compounds in water (EC European Commission, 2011). Metals studied here include: aluminium (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), lithium (Li), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). Metals occur naturally in the environment; however, the main sources in the environment include agricultural and industrial processes and their use as antifouling chemicals, corrosion anodes or on ship hulls or marine installations. Mercury, cadmium and lead are among the most toxic metals to humans and living organisms in general and, as other pollutants, they have been regulated by European Directives such as the Water Framework Directive (WFD) and their status assessment is often monitored in support of the Marine Strategy Framework Directive (MSFD) obligations.

Several sediment quality guidelines (SQGs) can be used for the assessment of the environmental status in coastal areas (e.g. Bakke et al., 2010; Bellas et al., 2008; Burton, 2002; Menchaca et al., 2012). In this study, the potential ecological risk of the sediments was evaluated using the approach of the US National Oceanic Atmospheric Administration (NOAA) (Long et al., 1995) based on the Effects Range Low (ERL) and the Effect Range Median (ERM) guidelines. In brief, contaminant concentrations below the ERL are not expected to produce adverse effects, while levels above the ERM are likely to be toxic. It is well recognized that SQG can be useful to identify anthropogenic inputs to the environment, nevertheless, both PAHs and trace metals can also have a natural origin. In this sense, different areas will present natural concentrations, so-called BCs that identify natural levels (OSPAR Commission, 2009). Establishing reference concentration (often called BCs) and/or the distance to target (an OSPAR principle related to the relation between the present concentration and the BC objective) is critical for remediation and management objectives, detecting contamination patterns, and developing monitoring programs for the contaminants of concern. Obtaining suitable background sampling locations can be challenging as samples should be collected from areas with similar physical, chemical, geological, and/or biological characteristics to the target area and not impacted by the chemical substances of interest. Easily accessible or local pristine areas, have gradually reduced in number and remote areas are now deemed to be suitable alternatives. In this regard, the Porcupine Bank fulfils the requirements to infer background values that can be used for evaluations in the North Atlantic.

Recognising the less impacted status of the Porcupine Bank sampling area, the objectives defined in this study were:

- To evaluate the concentration of PAHs and trace metals in sediments collected in the Porcupine Bank.
- To compare established OSPAR BC values with the data obtained from the Porcupine Bank.
- to establish whether these newly derived BC values correspond to other existing marine thresholds.
- to establish whether these newly derived BC values are appropriate.

## 2. Material and methods

### 2.1. Study area and sampling procedure

Surface sediment samples were collected using a *meso* box-core during a number of scientific cruises performed aboard R/V *Vizconde de Eza* in the years 2006 to 2012. Sampling locations and basic sediment characteristics are shown in Table S1 and Fig. 1.

Sediments were stored in clean appropriately prepared containers, deep-frozen on board prior to transport to the laboratory, where they were freeze-dried on arrival. Analyses were conducted in the total fraction of sediment (fraction <2 mm), consequently, the samples were sieved through a 2 mm mesh to remove the remains of shells and stones. The samples were then homogenised and stored in clean glass vials at room temperature until chemical analysis took place.

As the objectives of this study were to complete a wider contaminant status study and to derive BCs, an adequate sample volume for analysis and a wide knowledge of the sediment characteristics (including granulometric composition and content of organic matter (OM)) is paramount to determine the base characteristics of the sediments. The fraction <63 µm was determined using wet sieving and subsequent drying and weighing, to characterise the sediment and facilitate data assessment. The textural characteristics of the sediments will also be analysed against pollutant concentration in each sample to ensure the absence of correlation, thus confirming a non-biased concentration of pollutants due to the fine particles in the sediments (Long et al., 1995).

The OM content was determined using the combustion method described as weight loss of dried (100 °C, 24 h) samples after combustion (500 °C, 24 h) (Lourido et al., 2019). Also, the aluminium percentage and the Li concentration are presented in Table S1 since they can be used as an indicator of sediment mineralogy.

### 2.2. Analytical methods

PAHs and metals analysis were performed following previously described procedures. PAHs listed in Table 1 were determined following the procedure described in Viñas et al. (2009). In brief, around 3 g of the freeze-dried sediment were Soxhlet extracted and after a clean-up step using aluminium oxide and copper, the extracts were analysed using liquid chromatography (HPLC) with a fluorescence detector.

Analytical procedures for the determination of metals listed in Table 1 were described in detail elsewhere (Quelle et al., 2011). In summary, the analysis of all metals, excluding Hg, included total digestion of the samples with a mixture of hydrofluoric acid and *aqua-regia* in a microwave oven, followed by neutralisation with boric acid. Nitric acid digestion was applied for total Hg analysis. Selected metals were analysed using a Perkin-Elmer AAnalyst 800 spectrophotometer equipped with a Zeeman background correction device. The operational parameters and matrix modifiers were those recommended by the manufacturer. Total Hg was determined by cold vapor technique, employing a Perkin-Elmer FIMS-400 system (SnCl<sub>2</sub> as reducing agent).

The analysed metals were those that tend to be more associated to anthropogenic activities (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn). In addition, Al, Li and Fe were also determined to facilitate the recognition

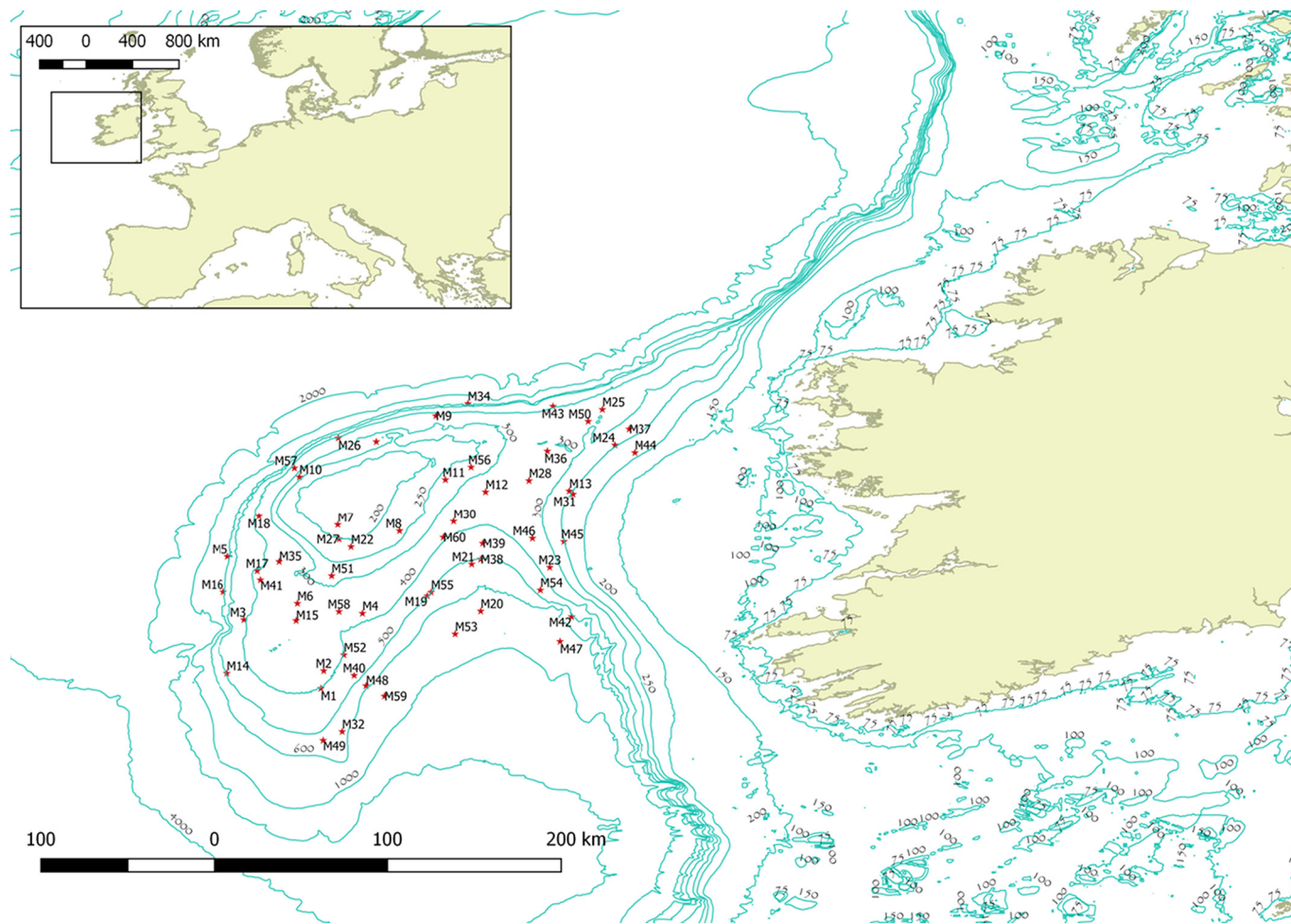


Fig. 1. Map of the Porcupine Bank showing sampling sites and bathymetry of the area.

of sediment trace metal variations caused by natural differences in sediment mineralogy. Metal concentrations are expressed in mg/kg dry weight (mg/kg d.w.) except for Al and Fe, whose units were mg/100 mg dry weight (i.e. the percentage of mass d.w.).

The analytical methods, PAHs and metals, were performed under a quality assurance scheme that was periodically checked. Protocols included analysis of certified reference materials, duplicate samples, blind samples, recovery procedures, procedural blanks and control charts, as well as regular satisfactory participation in international interlaboratory exercises, such as those organised by the QUASIMEME Interlaboratory Programme (Quality Assurance of Information for Marine Environmental Monitoring in Europe <https://www.wepal.nl/en/wepal.htm>). LOQ of the analytical methods are presented in Table 1.

The software used for statistical analysis was R Software version 3.4.3 (2017).

### 3. Results and discussion

#### 3.1. Sediments characterization

Samples were collected at a depth range comprised between a minimum of 193 m (M7) to a maximum depth of 738 m corresponding to the station M47 (Table S1), the percentage of sediment fine particles (<63  $\mu\text{m}$ ) varied from 1.46 % (M57) to 85.1 % (M19) of total sediment volume with an average value of 33.3 % (Table S1, Fig. S1). The organic matter (OM) content in the 2 mm fraction varied in a range of 0.67–5.66 % with an average of 2.63 % (Table S1, Fig. S2).

The sediment organic matter in the study samples is generally in accordance with the average quantity determined worldwide, ranging from 1 to 3 % (Blair and Aller, 2012; Mayer et al., 1988; Trask, 1955) In the studied area three locations were identified where both OM and percentage of sediment fine fraction (<0.63  $\mu\text{m}$ ) were higher than the wider general values obtained, these being the areas around station M21, M48 and a third one with a slightly lower value around station M41. All of these are located southwest of the studied area and at a depth of around 500 m.

Organic contaminants can be linked to the fine fraction of the sediment creating a modification of the concentration in those samples with coarse grains. The independence between the sediment's textural characteristic (grain size distribution) and organic contaminant concentrations was studied via the calculation of determination coefficients (Fig. S3). A weak correlation was derived for the organic matter presence with the fine fraction percentage ( $R^2 = 0.5578$ ), or the aluminium with the fine fraction ( $R^2 = 0.2963$ ) but it was confirmed a lack of correlation of organic pollutants with the fine fraction (e.g. for Pyr  $R^2 = 0.0227$ ).

Further, a non-parametric Kruskal-Wallis test was completed to compare the textural characteristics of the sediment (i.e. sampling depth, organic matter, aluminium content and grain size) with the concentration of studied contaminants (Table S4). The Kruskal-Wallis statistics ( $H = 153.6$ ,  $df = 2$ ,  $p = 0.000$ ) indicated that there is significant difference among the variables PAHs concentrations in sediments, OM and sampling depth. Furthermore, the regression coefficients (R) were generally <0.8 indicating a low-level correlation between each of the sediment characterization parameters and measured contaminant concentrations. Sampling depth has been documented to significantly affect the distribution of

**Table 1**

Analytical and assessment values of the studied pollutants. When the min value is under LOQ is indicated the percentage of samples that yield that result.

Name	Acronym	Analytical method	Analytical limit	Guideline/Threshold		Concentrations this study		
			LOQ	BC <sup>(REF)</sup>	ERL	MIN	MAX	ST DEV <sup>c</sup>
<b>PAHs<sup>a</sup></b>								
Phenanthrene	Phe	HPLC-FLD	0.08	17	240	0.48	7.90	1.72
Anthracene	Ant		0.03	3	85	<0.03 (19 %)	3.91	1.03
Fluoranthene	Fla		0.22	20	600	<0.22 (1,7 %)	5.61	1.38
Pyrene	Pyr		0.12	13	665	0.53	9.25	2.22
Benz[ <i>a</i> ]anthracene	BaA		0.10	9	261	<0.10 (15.5 %)	2.60	0.646
Chrysene	Chry		0.14	11	384	<0.14 (5.2 %)	3.57	0.931
Benzo[ <i>e</i> ]pyrene	BeP		0.28	N.A.	N.A.	0.43	4.22	0.913
Benzo[ <i>b</i> ]fluoranthene	BbF		0.18	N.A.	N.A.	0.46	6.02	1.29
Benzo[ <i>k</i> ]fluoranthene	BkF		0.13	N.A.	N.A.	<0.13 (1.7 %)	2.28	0.470
Benzo[ <i>a</i> ]pyrene	BaP		0.09	15	430	<0.09 (1.7 %)	1.76	0.374
Benzo[ <i>g,h,i</i> ]perylene	BghiP		0.15	45	85	0.47	3.70	0.727
Dibenzo[ <i>a,h</i> ]anthracene	DBahA		0.19	N.A.	N.A.	<0.19 (31 %)	0.83	0.230
Indeno[1,2,3- <i>c,d</i> ]pyrene	IP		0.29	50	240	0.36	6.19	1.32
Name	Acronym	Analytical method	Analytical limit	Guideline/Threshold		Concentrations this study		
			LOQ	BC	ERL	MIN	MAX	ST DEV <sup>c</sup>
<b>Metals<sup>b</sup></b>								
Aluminium	Al		0.0031	N.A.	N.A.	0.23	4.75	0.796
Arsenic	As		0.189	15.0	8.2	1.61	14.2	2.73
Cadmium	Cd		0.009	0.20	1.2	<0.009 (10 %)	0.177	0.047
Chromium	Cr		0.178	60.0	81	9.36	60.5	11.8
Copper	Cu		1.09	20.0	34	<1.09 (20 %)	14.9	3.44
Iron	Fe		0.007 %	N.A.	N.A.	0.53	2.66	0.390
Mercury	Hg		0.006	0.05	0.15	0.006	0.129	0.021
Lithium	Li		1.26	N.A.	N.A.	2.78	37.9	6.54
Manganese	Mn		0.471	N.A.	N.A.	86.3	304	43.9
Nickel	Ni		0.211	30.0	20.9	3.59	19.6	3.89
Lead	Pb		0.103	25.0	46.7	3.32	11.9	1.84
Zinc	Zn	AAS	0.682	90.0	150	5.43	63.7	12.28

LOQ: Limit of Quantification; BC: Background concentration; ERL: Effects range low; d.w.: dry weight. N.A.: not available.

REF: (OSPAR, 2014).

<sup>a</sup> Units for PAHs in µg/kg d.w.<sup>b</sup> Units for Fe and Al % rest of the metal in mg/kg d.w.<sup>c</sup> For calculatin the standard deviation, <LOQ data were supposed to be 0.

contaminants, so the potential for correlation among contaminants concentrations and depth was studied: only Li -among metals- and BbF -among the organic contaminants- show a slight correlation (Table S5). Organic matter and granulometry were also studied as possible factors influencing the retention of contaminants, the correlation between OM-vs-contaminants concentration and % granulometry-vs-pollutants concentration indicated that only in the case of Zn were both correlation factors >0.6 (Table S5). This points towards a non-correlation between pollutant's concentration and the fine fraction, with the proviso that, when measuring close to the detection limits, correlations can be difficult to identify.

### 3.2. Description of the area in terms of the presence of organic contaminants and trace metals

#### 3.2.1. Organic contaminants (PAHs)

PAHs can be of both natural or anthropogenic origin, the area sampled in this study has a great potential value to identify the influence of both sources. A key aim of this study is to provide information about the current PAH status in the Porcupine Bank and on the potential applicability of these data as BC concentrations.

The area is not subject to routine monitoring programs for PAHs, thus there is a lack of periodic information in terms of the presence and evolution of organic contaminants. Such information is valuable as it supports the description of the environmental condition of the area (e.g for OSPAR and/or MSFD Good Environmental Status -GES- assessment) and on the ultimate fate of PAHs in open ocean environment.

In the samples analysed the sum of 13 PAHs ranged from 5.26 to 51.1 µg/kg d.w. with none of the individual PAHs determined in concentrations in excess of 16 µg/kg (Table S2). The measured concentrations of

individual PAHs were then compared with internationally recognized ERL threshold values (Table 1). For all sampling stations, concentrations of 9 individual PAHs (those with defined ERLs) were all between 2 and 3 orders of magnitude below corresponding ERL values, therefore, it can be concluded that PAHs in sediments from these sites present almost no ecological risk to resident organisms.

The data obtained in this study, were then further compared to PAHs concentrations determined in different locations around the world (Table 2), confirming the very low-level prevalence of PAHs in sediments from the Porcupine Bank. Concentrations of the sum of PAHs determined in the present study were under 51.1 µg/kg d.w., with, for example, samples from remote areas of the Barents Sea, Black Sea, or some regions in China yielding values over 200 µg/kg d.w. In addition, the lowest values determined in this study (~5 µg/kg d.w.) were similar to those found in some samples of the Galician continental shelf (NW Spain) or open areas in France. Moreover, it should be noted that sites in literature with low concentrations, similar to those determined in this study, often also exhibited samples with much higher concentrations (around 10 times higher ~300–800 µg/kg), no such variation was evident in this Porcupine Bank study. For additional context, only one study (from 33 other similar literature sources) performed on the Argentine Continental Margin (ACM) of the Argentinean Economic Exclusive Zone (EEZ) from 41°30'S to 48°S (Portela et al., 2012) exhibited concentrations for the sum of 13 PAHs similar to the values determined in the Porcupine Bank.

#### 3.2.2. Trace metals

As described for PAHs, metals can have both natural or anthropogenic origin and are found in oceans, rivers and soil; however anthropogenic inputs have increased their content around the world. As they are not

**Table 2**

Review of PAHs values presented for different areas. The number of PAHs analysed in each case is indicated. An \* indicates when naphthalene was one of the PAH determined and, if available, the concentration is given in brackets. In all the studies the concentrations were not corrected or normalized to organic carbon and are expressed as  $\mu\text{g}/\text{kg}$  dry weight.

Region	Area	Range $\Sigma$ PAHs ( $\mu\text{g}/\text{kg}$ d.w)	Reference	
Bay of Biscay, Iberian Coast and Ireland	Porcupine Bank ( $\Sigma_{13}$ PAHs)	5.26–51.06	Present study	
	England and Wales ( $\Sigma_{15}$ PAHs)*	26 (<13)–43,470 (2430)	Woodhead et al., 1999	
	Ría Santander, Spain ( $\Sigma_{16}$ PAHs)*	42.16 (8.98)–20,243 (97.5)	Pérez-Fernández et al., 2019	
	Ría Arousa, Spain ( $\Sigma_{16}$ PAHs)*	23 (0.8)–6647 (35.9)	Pérez-Fernández et al., 2015	
	Ría de Vigo, Spain ( $\Sigma_{13}$ PAHs)	29–3203	Viñas et al., 2009	
	Galicia continental shelf, Spain ( $\Sigma_{13}$ PAHs)	0.9–422	Franco et al., 2006	
	Santander Bay, Spanish( $\Sigma_{16}$ PAHs)** <sup>a</sup>	20 (<LOD)–344,600 (2700)	Viguri et al., 2002	
	France( $\Sigma_{14}$ PAHs)	4–855	Soclo et al., 2000	
	North Sea	Norway ( $\Sigma_{16}$ PAHs)*	29 (3.2)– 1129 (178)	Boitsov et al., 2020
		Norwegian Sea, Norway ( $\Sigma_{22+8}$ PAHs)*	9.5 (<0.5)–4610 (83)	Boitsov et al., 2013
SW Barent Sea, Norway ( $\Sigma_{22+8}$ PAHs)*		20.0 (0.68)–363 (2.46)	Boitsov et al., 2009	
Northwestern Black Sea ( $\Sigma_{14+3}$ PAHs)		52.6–269	Maldonado et al., 1999	
Aegean Sea ( $\Sigma_{18}$ PAHs)		8.98–113	Hatzianestis et al., 2020	
Mediterranean Sea	Mediterranean coast, Israel ( $\Sigma_{18}$ PAHs)*	11.8 (1.7)–190.1 (2.4)	Astrahan et al., 2017	
	Mediterranean Sea, France-Spain ( $\Sigma_{14}$ PAHs)	0.32–8400	Baumard et al., 1998	
	NW Mediterranean Sea, France-Italy ( $\Sigma_{14}$ PAHs)	86.5–48,090	Benlahcen et al., 1997	
	Pearl River Estuary, China ( $\Sigma_{16}$ PAHs)*	156 (10.77)–9220 (50.15)	Fu et al., 2001	
Asia	Pearl River, China ( $\Sigma_{16}$ PAHs)*	331(33)–10,811(609)	Mai et al., 2002	
	South China Sea ( $\Sigma_{11}$ PAHs)*	24.7 (3.8)–275.4 (34.7)	Yang, 2000	
	Xiamen Harbour, China ( $\Sigma_{16}$ PAHs)*	247 (1)–480 (<1)	Zhou et al., 2000	
	Kyeonggi Bay, Korea ( $\Sigma_{24}$ PAHs)*	9.1–1400	Kim et al., 1999	
	Masan Bay, Korea ( $\Sigma_{16}$ PAHs)*	41.5–1100	Khim et al., 1999	
	America	Michigan Lake, USA ( $\Sigma_{16}$ PAHs)*	<50–16,900	Kannan et al., 2005
Todos Santos Bay, Mexico ( $\Sigma_{16}$ PAHs)		7.6–813	Macias-Zamora et al., 2002	
S. Carolina Estuary, USA ( $\Sigma_{28}$ PAHs)*		33–9600	Kucklick et al., 1997	
San Francisco Bay, USA ( $\Sigma_{16}$ PAHs)*		2564 (290)–27,170 (1650)	Pereira et al., 1996	
Kitimat Harbour, Canada ( $\Sigma_{16}$ PAHs)		310–528,000	Simpson et al., 1996	

biodegradable, they tend to accumulate in the environment associated with organic and inorganic matter. Also, it is well known that metal concentrations in sediments can present natural variations as a function of sediment characteristics such as grain size.

In this study, the concentrations of metals in sediments are presented in Table 1 (and Table S3) in parallel with the applicable Effects Range Low (ERL) guideline for each metal. As can be observed, some metal concentrations were below sensitive quantification limits with the conclusion that, overall metal levels were very low in Porcupine Bank samples.

The concentrations of all the studied metals, except for As, were below the defined ERL value, which indicates that they were not expected to produce adverse effects on aquatic organisms. The As concentration in 11 of 60 stations exceeded the ERL specific value (8.2 mg/kg d.w.). However, worldwide studies show a different behaviour of As compared with other metals and although the values exceed the guideline values this can often be attributed to natural enrichment, like rock weathering and soil formation, increasing As values due to a non-anthropogenic input.

The OSPAR Commission, aware of this phenomenon, indicated that the ERL/ERM values for As are too low for their application in the status assessment of European coastal areas. Moreover, the BC expected in pristine/remote areas, proposed by the OSPAR Commission (15 mg/kg d.w.) (OSPAR Commission, 2009) is 2 times higher than the defined ERL. Taking this into account it has been concluded that As determined in the Porcupine Bank samples is low since the highest As concentration in Porcupine Bank samples (station M34 14.20 mg/kg d.w.) is lower than the defined OSPAR BC.

To put the present data into perspective, they were compared to trace metal concentrations in sediments from similar studies for different areas (Table 3). As expected, the remoteness of the study area is reflected in the concentration of the metals analysed. Sampling sites were many kilometres away from any known anthropogenic input, so sediments were not expected to be contaminated at most stations.

Due to geographical proximity they are compared with those reported by Callaway et al. (2011) and Charlesworth and Service (2000) for different areas of Ireland, with those from Porcupine Bank being much lower. They are also lower than those obtained in sediments sampled in the English Channel (Hamdoun et al., 2015).

Table 3 also lists a number of studies carried out in sediments from global remote locations such as Azores Platform (Palma et al., 2013) or the Argentine Continental Margin (ACM) (Portela et al., 2012). A comparison of these data with those found in sediments from global isolated locations confirms the low levels in the Porcupine Bank.

Deep-sea sediments studied in the Azores Platform in the North-East Atlantic region presented concentrations of As in the range of 0.54–3.9 mg/kg d.w.; for Cr 2.1–39 mg/kg d.w.; Li 1.9–13 mg/kg d.w. and Pb <0.2–7.4 mg/kg d.w. These values are somewhat lower than those found in the Porcupine area but with concentrations of Cu (8.6–28 mg/kg d.w.); Zn (4.6–91 mg/kg d.w.) and Mn (85–1395 mg/kg d.w.) being lower in Porcupine than in the Azores platform. Again, arsenic variations can be explained because of an enriched process due to the rock weathering process (Zhao et al., 2020) or potentially due to biological activity disturbing the sediment, resulting in a higher background value (Zhao et al., 2020).

The expansive Argentine Continental Margin (ACM) study found concentrations for As (2.65–18.90 mg/kg d.w.), Cu (<2.00–14.50 mg/kg d.w.), Ni (1.62–18.80 mg/kg d.w.), Zn (17.70–7240 mg/kg d.w.) and Hg (<0.001–0.113 mg/kg d.w.) similar to the ones determined in the Porcupine Bank with the concentrations of Cd (0.022–0.291 mg/kg d.w.), Cr (8.03–230 mg/kg d.w.), Fe (1.18–6.74 %), Li (7.74–46.80 mg/kg d.w.) and Mn (204–734 mg/kg d.w.) being lower in the Porcupine Bank than in the ACM.

### 3.3. Applicability in support of BC values

Establishment of “background” status to a sampled area involves a number of steps including confirmation of the remote/pristine nature of the sampling site, completion of a wide-scale review of data from previously established baseline locations (e.g. from sediment cores, deep sediments) through to the assessment of the test site data relative to established Ecological or other relevant thresholds.

As previously discussed, the studied area exhibits a varied bathymetry, samples were taken from 193 m depth (M7) to a maximum depth of 738 m (M47); also, the percentage of sediment fine particles (<63  $\mu\text{m}$ ) varied from

**Table 3**  
Review of trace metal concentrations presented for different areas. The concentrations are expressed in mg/kg d-w- except for Fe and Al in %.

Region	Area	Al%	As	Cd	Cr	Cu	Fe%	Hg	Li	Mn	Ni	Pb	Zn	Reference
Iberian Coast, English Channel and Ireland	Porcupine Bank	0.23–4.75	1.61–14.2	<0.009–0.177	9.36–60.5	<1.09–14.9	0.53–2.66	<0.006–0.079	2.78–37.9	86.3–304	3.59–19.6	3.32–11.9	5.43–63.7	Present study
	Ría de Vigo, Spain			0.035–1.08		0.883–165		0.012–0.656			2.00–47.6	8.72–268	11.7–348	Quelle et al., 2011
	Ría de Pontevedra, Spain			0.058–1.34		3.09–88.8		0.006–1.93			1.00–29.0	13.8–145	13.9–227	Quelle et al., 2011
	Bilbao estuary, Spain			0.5–16.2		37–585					17–109	48–689	149–2192	Irabien et al., 2018
Gulf of Cádiz, Spain		<0.031–8.92	14.6–692	<0.009–3.50	2.4–108	2.80–1477	0.07–8.08	<0.006–3.61	2.4–78.7	53.3–647	1.77–50.5	1.65–692	3.1–1726	Besada et al., 2022
	Azores Platform, North East Atlantic	0.43–9.0	0.54–3.9		2.1–39	8.6–28	0.052–6.3		1.9–13	85–1395	<2–17	<0.2–7.4	4.6–91	Palma et al., 2013
	Beaufort's Dyke, Irish Sea	1.55–8.10	10.67–41.97	<0.200–0.502	38.99–84.59	7.93–16.47	1.76–3.78	<0.025–0.05	14.94–90.07	562–2946	10.69–33.49	8.89–29.34	43.92–108	Callaway et al., 2011
	Belfast Lough Northern Ireland	3.1–5.6			67–333	9.0–104	1.1–3.8	0.04–0.88			8.6–65.6	19.6–134	54–407	Charlesworth and Service, 2000
Strangford Lough Northern Ireland		2.8–6.3			38–125	5.1–51.9	1.1–4.0	0.03–0.72			11.2–42.0	14.6–1546	12–144	Charlesworth and Service, 2000
	Carlingford Lough Northern Ireland	2.3–5.4			53–91	3.5–36.2	0.6–3.4	0.04–0.32			6.9–36.2	18.1–48.3	24–163	Charlesworth and Service, 2000
North Sea	English Channel	1.3–2.5	6–42	1–4	9–74	10–254		0.01–0.43			9–27	9–263	24–327	Hamdoum et al., 2015
	Norwegian sediments, Norway			0.04–0.31							8.1–57.3	11.12–118	20.0–311	Everaert et al., 2017
Mediterranean Sea	Coles Bay Area, Svalbard		1.74–6.99	1.19–3.50		1.63–9.40		1.17–5.26				16.3–188	0.06–4.83	Leung et al., 2021
	Valencia coastline, Spain		2.71–36.2	0.11–0.29	4.64–29.0	1.18–6.53		0.01–0.18			1.92–17.0	2.19–9.33	8.72–57.1	Pachas et al., 2019
Asia	Golfe Juan Bay, France		2.50–11.6	0.05–0.56	1.5–17.8	17.9–79.6				43.3–194	2.8–271	30.5–235	29–217	Tiquio et al., 2017
	Campania, Italy		12.3–100	0.0–0.7	0.5–49.5	3.5–86.2	10.5–66.8	0.0–25.3		20–1353	0.0–35.4	11.5–378	42.1–867	Trifuoggi et al., 2017
	Algerian coast, Algeria		8.6–57.9	0.06–0.53	18.1–169	2.5–48.6	0.77–5.04			193–728	6.4–59.2	6.6–68.3	17.4–234	Ahmed et al., 2018
	Nearshore coast, China Mainland		1.82–88.3	0.010–9.50	3.63–389	0.300–794		0.002–1.39			5.00–135	0.130–180	1.01–1008	Liu and Yu, 2022
America	Great Bay Area, China		1.74–34.0	1.19–9.23		14.1–382		0.05–0.312				23.3–538	2.63–161	Leung et al., 2021
	Korea	2.3–12.6			6.8–117	4.7–100	1.2–5.7	16–165			8.1–45.5	11.5–91.4	22–312	Song et al., 2014
	Cau Hai lagoon, Vietnam		6.00–20.0	0.200–0.400	44.0–98.0	8.00–20.0					14.0–32.0	23.0–53.0	47.0–123	Tran et al., 2018
	Pacific Ocean, Palau		0.9–43.5	0.001–0.052	4.9–451	1.1–66.4		0.002–0.070	1.3–59.1		5.1–67.9	0.1–2.7	0.7–52.5	Jeong et al., 2021
America	Coramandal Coast, India			3.30–19.8	57.75–109	27.50–76.45	2.13–70.78				7.38–27.98	2.67–49.63	8.55–78.76	Anbusevan et al., 2018
	Argentina Economic Exclusive Zone (EEZ)	1.57–8.10	2.65–18.90	0.022–0.291	8.03–230	<2.00–14.50	1.18–6.74	<0.001–0.113	7.74–46.80	204–734	1.62–18.80	2.37–30.90	17.70–72.40	Portela et al., 2012
	Nova Scotia, Canada		0.50–62.00	0.05–3.80	1.00–305	0.50–220	0.003–1.850				2.00–697	0.73–583	5.00–2300	Zhang et al., 2019
	Kachemak Bay Alaska, USA	6.24–8.55	8.93–48.6	0–0.24	59.3–147	20.1–69.4	3.19–6.10	0.05–1.07		467–1080	28.5–56.5	4.73–15.2	74–158	Apeti and Hartwell, 2015
Galveston Bay, Texas, USA	1.63–82.75	1.3–20.0	0.02–0.5	1.5–70.8	0.8–77.0	0.64–50.30	0.004–0.40		6.1–695	1.1–30.3	1.8–29.2	4.3–195	Lopez et al., 2022	

1.46 % (M57) to 85.15 % (M19) with an average value of 33.3 % (Table S1, Fig. S1) and the organic matter (OM) content range 0.67–5.66 % with an average of 2.63 % (Table S1, Fig. S2). The remoteness of the test site located ~200 km offshore further coupled with the prevailing climatic aerial deposition characteristics (i.e. primarily SW airflow) and the deep-water nature of the derived sediment sample qualifies the test samples as being lowly impacted relative to nearer shore shallow water samples.

Background values determined for PAHs and individual metal(loid)s in previous studies are presented in Table S6a and S6b respectively. Porcupine Bank sediment data evaluation in this study has concluded that PAH and metals values are all under or very close to previously published concentrations, and so can be deemed to represent a set of specific BC values for the area.

Overall the low-level PAH and metals results, comparison to existing data and relevant thresholds and the supporting information on the remote nature of the samples support these Porcupine Bank samples as being appropriate for the establishment of background concentrations, particularly so to perform North Atlantic evaluations, since they yield very low concentrations in a range of samples over a diverse OM content and granulometry range.

All sediments were determined to have similar or lower concentrations for PAHs and metals compared to previously defined BC values (OSPAR Commission, 2008; Pérez-Fernández et al., 2019, see Figs. 2 & 3).

It should be noted that derivation of background criteria, as described by OSPAR, requires the normalisation of contaminant data to sediment co-factors such as organic matter (PAH) or lithium or aluminium (metals). Due to underlying geological considerations, normalisation of Iberian sediment environment for the derivation of OSPAR background values is not performed. Normalisation of Porcupine Bank data was not performed during this work but that data suggest that the values are lower than (or close to) the BC defined for the Spanish area by Pérez-Fernández et al. (2019), which are not normalized.

A final step was completed on the Porcupine Bank data utilizing an EC approach (EC European Commission, 2011) to infer BC concentration from a set of concentration values. This approach proposes that the 10th percentile of all remote location data is sufficiently robust to be deemed as a background concentration. The generation of 10th percentile data during this study plus the comparability of non-normalized Iberian data further supports the applicability of concentrations from the Porcupine Bank as being appropriate for background concentrations. Background concentrations derived during this study as well as the existing BC values accepted by OSPAR are summarised in

Table 4 and Table S6. While consideration needs to be given to the potential requirement for normalisation of Atlantic water test data (as per Baltic and/or North Sea), this study now reports a unique dataset that is particularly relevant to the completion of North Atlantic status evaluations.

#### 4. Conclusions

This study presents a wide spatial evaluation of the presence of a range of PAHs and trace metals in the Porcupine Bank. The deep-water nature of the sampling programme and the relative remoteness of the area from anthropogenic impacts has meant that few data exist but that the area can be deemed as a perfect location to assess the natural background concentrations of PAHs and metal(loid)s at a regional scale and to set up limits for the distinction between natural concentrations and those derived from anthropogenic contamination, especially suitable for the North Atlantic region. Concentrations at both a 10th percentile range in addition to comparison to existing literature data demonstrate the low levels of PAH and trace metals in sediments from this area. It was further concluded that the concentrations of both PAHs and trace metals are not expected to produce adverse effects on aquatic organisms and they are in range with those values obtained in remote areas.

While consideration needs to be given to the relevance of additional normalisation techniques to the date this study provides valuable and rare data from this dynamic environment and validates the recognition of the area as a reference location for the North Atlantic.

#### CRediT authorship contribution statement

**Lucía Viñas:** Conceptualization, Formal analysis, Investigation, Writing – original draft, Supervision, Funding acquisition. **Begoña Pérez-Fernández:** Formal analysis, Writing – original draft, Visualization. **Victoria Besada:** Formal analysis, Writing – original draft, Supervision, Funding acquisition. **Jesus Gago:** Formal analysis, Writing – original draft. **Brendan McHugh:** Formal analysis, Writing – original draft. **Santiago Parra:** Investigation, Writing – original draft.

#### Data availability

We have shared the data at Supplementary Material.

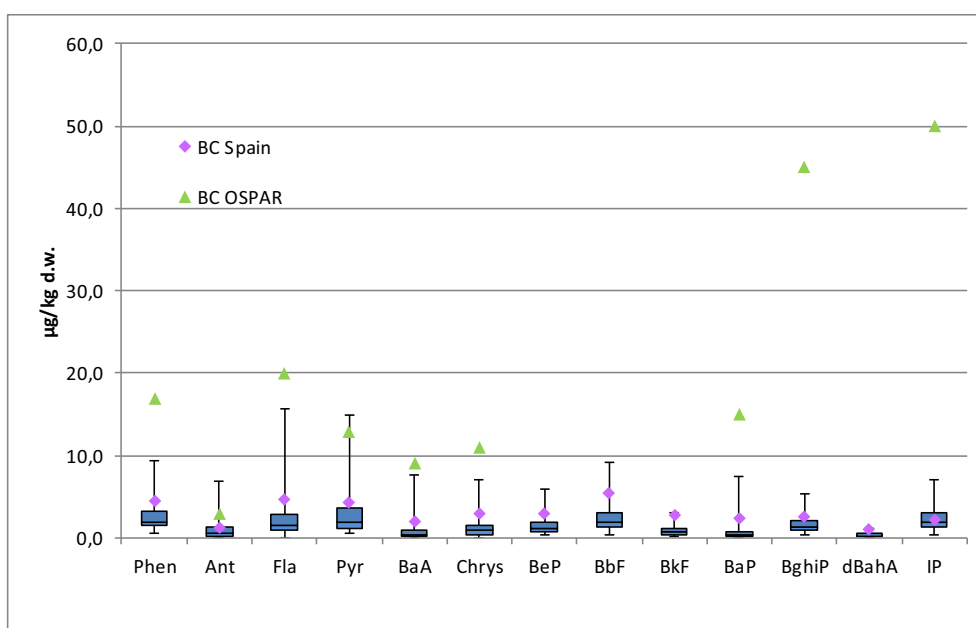


Fig. 2. Box-plot representation of PAHs concentration and comparison with published BC values.

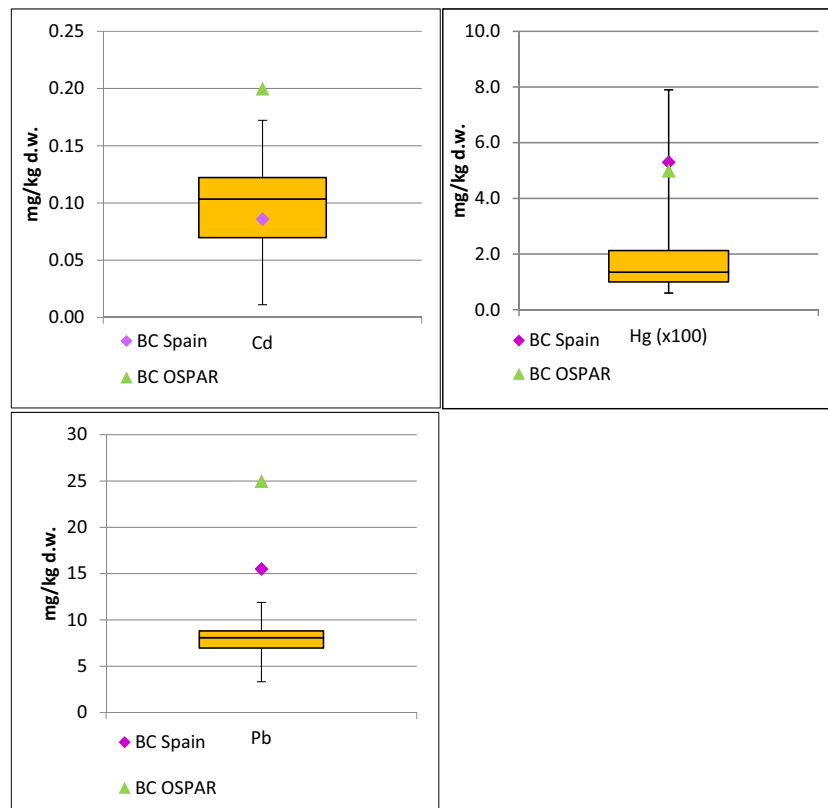


Fig. 3. Box-plot representation of Hg, Cd and Pb concentrations and comparison with published BC values.

#### 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.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.159189>.

Table 4

Derived BC values using the 10th percentile approach.

PAHs ( $\mu\text{g}/\text{kg d.w.}$ )	Proposed BC	Metal(oid)s ( $\text{mg}/\text{kg d.w.}$ )	Proposed BC
Phen	0.90	As	2.60
Ant	<0.03	Cd	0.01
Fla	0.59	Cr	20.8
Pyr	0.69	Cu	<1.09
BaA	<0.10	Fe	0.85
Chrys	0.23	Hg	0.01
BeP	0.64	Li	10.9
BbF	0.90	Mn	145
BkF	0.35	Ni	6.25
BaP	0.17	Pb	5.61
BghiP	0.72	Zn	19.7
dBahA	<0.19		
IP	1.12		

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