

Polycyclic Aromatic Hydrocarbon Composition of Sediments in the Ría de Vigo (NW Spain)

L. Viñas · M. A. Franco · J. J. González

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Abstract Individual parent polycyclic aromatic hydrocarbons (PAHs) were identified and quantified in samples of recent sediments at 32 stations in the Ría de Vigo (NW Spain) and its adjacent shelf by high-performance liquid chromatography and a fluorescence detector. This area suffers the pressure of nearly 500,000 inhabitants and includes a number of important marine organisms. The total concentration for the sum of the 13 PAHs quantified were in the range 28–3203 ng/g. The highest concentrations were found near the city of Vigo, where marinas and dockyards as well as highways with a high traffic flow are established. Low PAH concentrations were determined in the outermost part of the estuary, far from the anthropogenic influence. PAH isomers concentration ratios were assessed, indicating that the main source of these compounds in the whole area is pyrolysis. When compared with the EACs, threshold effect level, and probable effect level values, only the samples from the inner part of the ría can occasionally present adverse biological effects due to the PAH concentrations.

Polycyclic aromatic hydrocarbons (PAHs) are widespread chemical pollutants that can be introduced into the environment by various processes, including incomplete combustion at high temperatures of recent and fossil organic matter (pyrolytic origin), slow maturation of organic matter under geochemical gradient conditions (petrogenic origin), and short-term diagenetic degradation

of biogenic precursors (diagenesis), with most environmental inputs being linked with anthropogenic activity (Soclo et al. 2000).

Because of their low aqueous solubility and hydrophobic nature, PAHs tend to associate with particulate material. Subsequent particle deposition in rivers and coastal waters can lead to an accumulation of PAHs in sediments. Additionally sediments with high organic carbon content have the potential to accumulate significant concentrations of PAHs. Sediments having smaller particle size and a larger surface/volume ratio tend to accumulate PAHs to a larger extent than coarser, sandy sediments (Law and Biscaya 1994; Webster et al. 2001).

In this study, 13 parent PAHs were quantified, ranging from the triaromatics to the hexa-aromatics: phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chry), benzo[*e*]pyrene (BeP), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*ghi*]perylene (BghiP), dibenz[*a,h*]anthracene (DBaA), and indeno[1,2,3-*cd*]pyrene (IndP).

The focus of the study was the wedge-shaped Ría de Vigo, the southernmost estuary in the Rías Bajas (northwest Spain). The ría is orientated in a northeast to southwest direction, with a width from 600 m in the Rande Straits to more than 5 km at the mouth, where the Cíes Islands partially close off the estuary.

The area has a high level of primary productivity (260 g of carbon/m/year) (Cabanas López 1999; Fraga 1976) due to an intense outflow of nutrients and a positive estuarine circulation. The area comprises more than 500,000 inhabitants, most of whom (300,000+) live in the city of Vigo, which is located at the south of the estuary. Vigo has a significant port operation in addition to having moderate industrial development.

L. Viñas (✉) · M. A. Franco · J. J. González
Instituto Español de Oceanografía, Vigo Coastal Centre,
P.O. Box 1552, Vigo, Spain
e-mail: lucia.vinas@vi.ieo.es

All of these factors combined with geographic and oceanographic characteristics that restrict good oceanic water exchange could result in an accumulation of certain contaminants within the estuary.

Moreover, few studies have been completed detailing hydrocarbon levels in the sediments from this region (Viñas et al. 2002), with data tending to only be available in the aftermath of the Prestige incident and/or being restricted to the adjacent platform and the nearby rias (Franco et al. 2006; Mariño Balsa et al. 2003; Morales-Caselles et al. 2007; Salas et al. 2006).

Experimental

Sediment Sampling

Individual sediment samples prior to the Prestige oil spill incident were collected by box-corer dredge on board the Research Vessel (R/V) *José M^a Navaz* along the north and south margins of the Ría de Vigo and in its adjacent shelf (Fig. 1). Corresponding coordinates and sampling depths are reported in Table 1. The superficial sediment (0–2 cm) was collected and frozen on board and then freeze-dried in the laboratory. The sediment fine fraction was subsequently determined by wet sieving on a 63 μm sieve and the total organic carbon content was measured

by wet oxidation with potassium dichromate on freeze-dried sediments.

Determination of PAHs by HPLC-FLD

Each sediment sample (<2 mm) was thoroughly homogenized and an aliquot (~4 g) was removed for the determination of water content by oven-drying at 110°C for 24 h. A second aliquot of sediment (3–7 g) was extracted in a Soxhlet apparatus using hexane–acetone (3:1 in volume) (Franco et al. 2006; Viñas 2002; Viñas et al. 2002). The extract was concentrated in a rotary evaporator and then cleaned up using column chromatography with deactivated alumina with hexane elution. Sulfur precipitation was prevented by a copper turnings treatment.

The concentration and composition of the PAHs were determined by high-performance liquid chromatography–fluorescence detector (HPLC-FLD) using a HP 1100 Series HPLC with a HP 1046 FLD or with wavelength programming (Agilent Technologies, Palo Alto, CA, USA). A Vydac 201 TP column (25 cm \times 0.4 cm and 5- μm particle size; Grace Vydac, Hesperia, CA, USA) was used.

The elution solvent used was a gradient of methanol and water and the column temperature was fixed at 23.5°C.

The FLD was set to vary the excitation and emission wavelengths along the period of the analysis in order to fix the conditions for each PAH. A degasser (Agilent

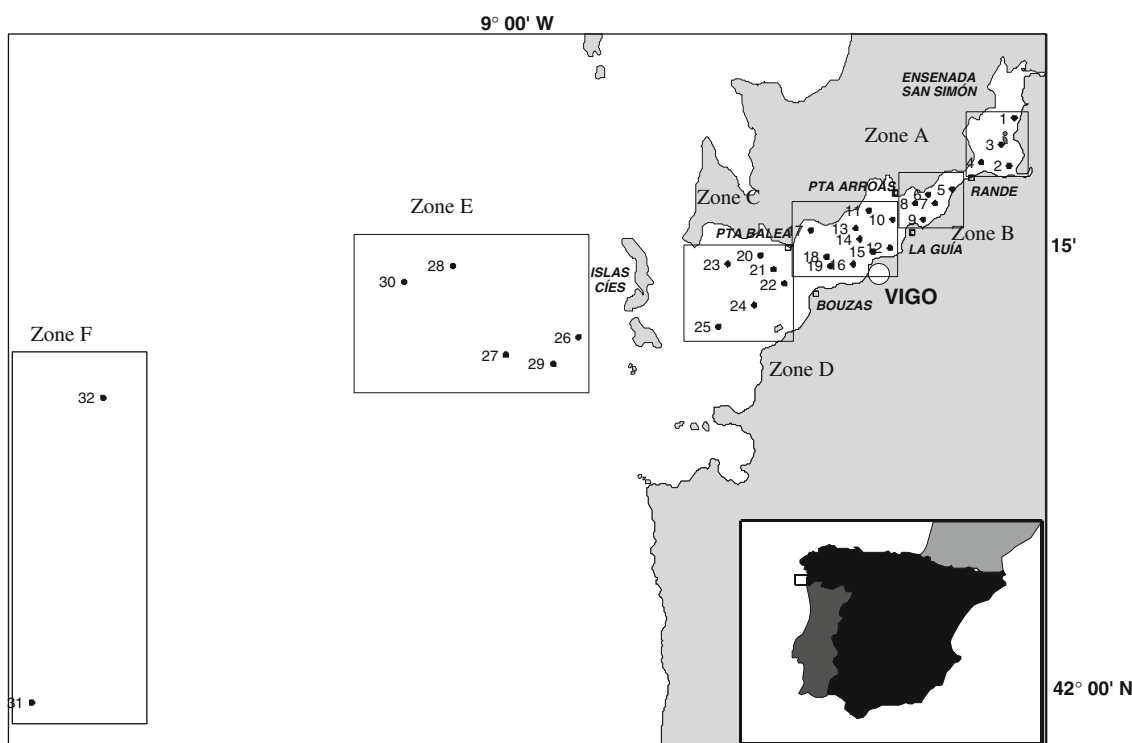


Fig. 1 Map of the Ría de Vigo, showing the location of the stations sampled. The area was divided into six zones

Table 1 Characterization of the stations

Station	Depth (m)	Latitude	Longitude	% <63 μm	% TOC
SR1	1	42° 19.2' N	8° 37.4' W	66.7	6.75
SR2	4	42° 17.6' N	8° 37.6' W	92.3	4.38
SR3	4	42° 18.3' N	8° 38.0' W	95.4	5.36
SR4	19	42° 17.7' N	8° 38.9' W	75.7	4.22
SR5	20	42° 16.8' N	8° 40.2' W	63.7	3.49
SR6	17	42° 16.6' N	8° 41.3' W	88.0	3.99
SR7	19	42° 16.3' N	8° 41.0' W	84.1	4.21
SR8	19	42° 16.3' N	8° 41.9' W	76.0	3.54
SR9	14	42° 15.8' N	8° 41.5' W	92.5	3.87
SR10	23	42° 15.8' N	8° 42.9' W	87.1	3.38
SR11	16	42° 16.1' N	8° 44.0' W	90.2	3.41
SR12	19	42° 14.8' N	8° 43.0' W	92.6	4.29
SR13	21	42° 15.5' N	8° 44.6' W	94.1	3.34
SR14	27	42° 15.1' N	8° 44.4' W	92.1	3.13
SR15	24	42° 14.7' N	8° 43.8' W	94.3	3.51
SR16	24	42° 14.3' N	8° 44.7' W	90.8	2.88
SR17	15	42° 15.4' N	8° 46.6' W	19.1	0.70
SR18	40	42° 14.5' N	8° 45.9' W	97.1	2.99
SR19	27	42° 14.2' N	8° 45.7' W	79.5	2.68
SR20	27	42° 14.6' N	8° 48.9' W	49.2	1.55
SR21	37	42° 14.1' N	8° 48.3' W	97.4	2.70
SR22	34	42° 13.6' N	8° 47.8' W	82.0	2.29
SR23	34	42° 14.3' N	8° 50.4' W	69.0	1.88
SR24	40	42° 12.9' N	8° 49.2' W	88.2	2.22
SR25	38	42° 12.2' N	8° 50.8' W	94.4	1.87
SR26	93	42° 11.8' N	8° 57.2' W	62.9	0.82
SR27	114	42° 11.2' N	9° 00.5' W	88.2	1.06
SR28	125	42° 14.2' N	9° 02.9'	54.2	0.87
SR29	98	42° 10.9' N	8° 58.3' W	62.2	0.80
SR30	130	42° 13.7' N	9° 05.1' W	42.1	0.77
SR31	450	41° 59.5' N	9° 22.0' W	33.5	0.61
SR32	216	42° 09.8' N	9° 18.8' W	28.5	0.41

Technologies, Palo Alto, CA, USA) was used to eliminate the air in the solvents, in order to prevent oxygen quenching effects.

Two certified solutions: PAH Mix 9 (containing 10 mg l⁻¹ of all 16 EPA's PAHs) and BeP (10 mg l⁻¹) were used in the quantification, using a multilevel calibration at five points in the range between 25 and 350 ng/g for each of the compounds. 2-Methyl-chrysene was employed as an internal standard.

Regular Laboratory Reference Materials (LRM), procedural blanks, blind samples, and duplicates were analyzed under the same conditions as the samples. The limit of detection, calculated as three times the standard deviation of the mean value of six procedural blanks, was found to be <0.1 ng/g for Phen, Ant, BaA, and BaP, between 0.1 and

0.2 ng/g for Pyr, Chry, BbF, BkF, BghiP, and DBaH, and between 0.2 and 0.3 ng/g for Fl, BeP and InP.

Recoveries in the reference materials were >80% and good reproducibility was achieved for individual PAHs (variation coefficient <6%). Further quality control was assured through successful participation in the QUASI-MEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) PAH program in which |Z| scores between ± 2 have been reported, indicative of internationally recognised satisfactory laboratory performance.

Chemicals and Reagents

The HPLC-grade solvents used (hexane, acetone, acetonitrile, and methanol; Merck, Darmstadt, Germany) were concentrated to a small volume and tested for PAHs. The water was purified in a Milli-Q Gradient Ultrapure Water System (Millipore). Copper turnings (>99.0% purity; Fluka) were activated by hydrochloric acid and then rinsed with water and acetone.

The certified solutions used for calibration (PAH Mix 9 and BeP) as well as 2-methyl-chrysene, used as the internal standard, were supplied by Dr. Ehrenstorfer GmbH (Angsburg, Germany).

Results and Discussion

Sampling points (Fig. 1) in the Ria de Vigo were located along a central axis with two transects to the north and to the south of the axis, with sites being selected in order to reflect a variation in potential PAH inputs. In order to facilitate the interpretation of the results, some additional parameters (granulometry and total organic carbon) were determined for each sample (see Table 1). The estuary was subdivided into six areas (shown in the map) for data management purposes (see Fig. 1).

Total PAH concentrations ($\Sigma 13$ PAHs) in the 32 sediments ranged from 27.7 ng/g dry weight (SR32 in the outermost zone F) to 2448 ng/g dry weight (SR5 in the zone B), with a mean across all samples of 983.4 ng/g dry weight (SD = 855.6 ng/g dry weight, $n = 32$).

A clear gradient for the PAH concentrations can be observed in Fig. 2, where for each zone, the minimum and maximum values have been represented, in addition to the first and third quartiles. The highest PAH levels were found in zone B samples, with levels descending toward zones E and F in the outer part of the estuary, these being further from probable PAH inputs such as dockyards and other industrial activities and from the most populated areas.

The city of Vigo is in the vicinity of zone B, but the water circulation in this "ría," in general terms, enters

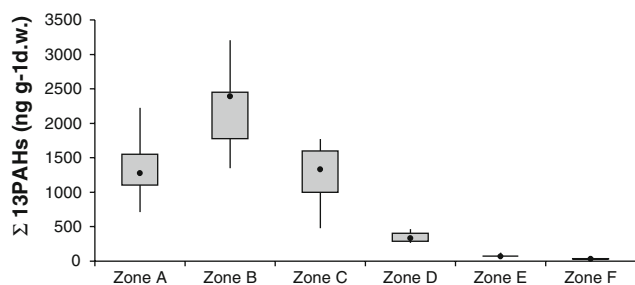


Fig. 2 Box and whisker diagram showing the sum of 13 PAHs by area. The median is indicated by solid circles, with the upper and lower quartiles being the lines above and below. The vertical lines show the PAH concentration spread

along the southern exits along the northern margins. This fact could explain the PAH values found in the innermost area.

Figures 3 and 4 demonstrate the total PAH concentrations (in log scale) with respect to the particle size and organic matter content. There is poor correlation ($r^2 = 0.45$) between the PAH content and the particle size. Sediments with a smaller particle size (higher percentage for the $<63\text{-}\mu\text{m}$ fraction) tend to accumulate PAHs to a greater extent, but the values have a great degree of dispersion. PAH levels appear to be more influenced by the

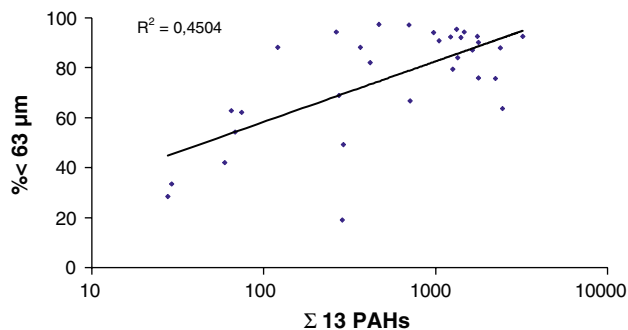


Fig. 3 Plot of the sum of PAHs versus the particle size ($\% <63\ \mu\text{m}$)

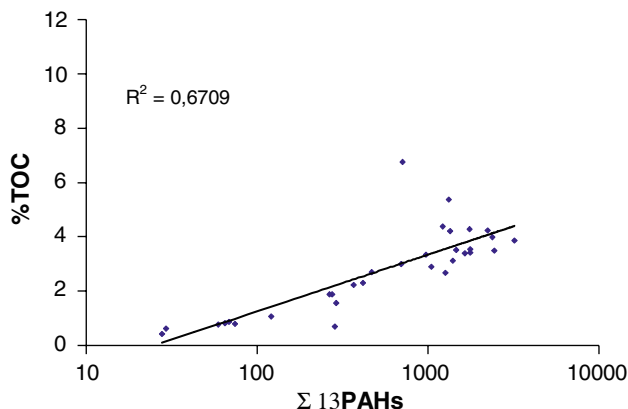


Fig. 4 Plot of the sum of PAHs versus the % TOC

organic matter content in sediments ($r^2 = 0.67$), as it has previously been reported for hydrophobic compounds such as PAHs (Webster et al. 2003).

Such relationships can partially explain PAH levels found in zone A (Ensenada de San Simón), where, despite the absence of important inputs, a significant PAH concentration were evidenced, probably due to its physicochemical properties: high % total organic content (TOC; mean = 5.18%, SD = 1.16%) and percentage for the $<63\text{-}\mu\text{m}$ fraction (mean = 82.53%, SD = 1.66).

Sampling was completed prior to the Prestige oil spill; therefore, the results presented herein are not influenced by the spill. In any case, the Prestige oil slicks never reached the inner part of the ría and the PAHs from the spill were found to be at low levels in zone E for the first months after the spill. Values were never found to exceed $60\ \mu\text{g}/\text{kg}$ dry weight for the sum of 13 PAHs, which is within the range observed in this work (Franco et al. 2006).

Polycyclic aromatic hydrocarbons have been analyzed and classed with regard to the number of structural rings: PAHs with three rings (Phen and Ant), PAHs with four rings (Fl, Pyr, BaA, and Chry), and PAHs with five and six rings (BeP, BbF, BkF, BaP, BghiP, DBahA, and IndP).

The percentage contribution of each PAH class to the total sum of PAHs is presented in Fig. 5. PAHs with five and six rings are generally the most abundant, closely followed by the four-ring class, both contributing 40–50% to the sum. The contribution of the three-ring class is around 10%, although the relative percentage increases as the sum of the 13 PAHs decreases. (For the three-ring class, there is a negative correlation with the sum of PAHs).

Petrogenic contamination is characterized by the predominance of the lower-molecular-weight (LMW) PAHs (tri–tetra aromatics) (Benner et al. 1990; Wise et al. 1988), whereas the higher-molecular-weight (HMW) PAHs dominate in the pyrolytic PAH contamination distribution

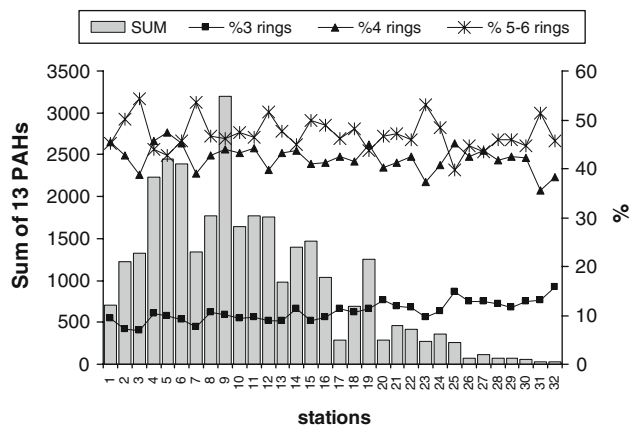


Fig. 5 Sum of 13 PAHs and percent values of contribution for each class of PAH

(Soclo et al. 2000). In this case, the relationship between LMW and HMW has been determined to be in the range 0.46–0.79, indicative of a pyrolytic origin pollution.

Polycyclic aromatic hydrocarbon concentration ratios are often used to distinguish between pyrolytic and petrogenic origins (Baumard et al. 1998a, 1998b; Webster et al. 2000). The most often used is the phenanthrene/anthracene ratio (Phen/Ant). Phenanthrene is the thermodynamically more stable isomer. The Phen/Ant ratio is temperature dependent and decreases with increasing temperature, so pyrolytic processes are characterized by low Phen/Ant values (<10) and the slow thermal maturation of organic matter in petroleum is characterized by much higher Phen/Ant ratios (>10). Similarly, the fluoranthene/pyrene ratio (Fl/Pyr) is often used to distinguish between pyrolytic and petrogenic sources. Values >1 are associated with pyrolytic origins.

In combination, the Fl/Pyr ratio when plotted against the Phen/Ant ratio (Baumard et al. 1999) enables the identification of a petrogenic and a pyrogenic zone. The zones defined by high Fl/Pyr ratios and low Phen/Ant were characteristic of pyrogenic PAHs. By plotting these ratios for the sediments it was clearly demonstrated that the main source of PAHs in this area was as a result of pyrolysis (Fig. 6). This finding was expected taking into account the population in the margins of this ría and that the degree of industrialization is quite high in the area. Additionally, the port of Vigo is one of the biggest in Spain, with a high level of maritime traffic. All those possible sources are usually related to a pyrolytic profile.

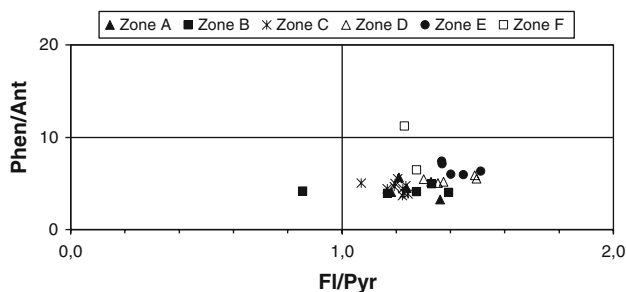


Fig. 6 Plot of the isomeric ratios Phen/Ant versus Fl/Pyr

One sediment sample from zone B (SR5) and a further sample from zone F (SR32) exhibited ratios outside of the pyrolytic and petrogenic zones. The SR32 sediment sample had the lowest sum of 13 PAH concentration (27.7 ng/g dry weight). The relatively low concentration of anthracene in this sediment resulted in a high Phen/Ant ratio that might be reflective of increased analytical error as the concentrations approach the limits of quantification. The sample SR5 is, nevertheless, one with the highest sums of 13 PAH concentration in this study; this station is situated near a shipyard and a motorway and therefore it is possible that this sediment has mixed source influences.

Overall fluoranthene was found to be the most abundant PAH, contributing $15 \pm 1.1\%$ to the sum of 13 PAHs. The box plot presented in Fig. 7 presents the contribution (median \pm sd) of each of the individual PAHs to the sum of 13 PAHs.

Table 2 presents PAH concentrations from the Ría de Vigo and other similar areas as reported in the literature. PAH levels found in Ría de Vigo are in the “normal” range for estuarine areas in Europe and America. The concentrations of PAHs from the Ría de Vigo are higher than those reported from the Mediterranean Sea, although the maximum values are not as high as in other regions (Baumard et al. 1998b; Botello et al. 1998; Kucklick et al. 1997; Pereira et al. 1999; Woodhead et al. 1999; Yim et al. 2005).

In order to assess whether these concentrations determined in this study pose a potential risk to the ecosystem, they have been compared (Table 3) with the Ecological

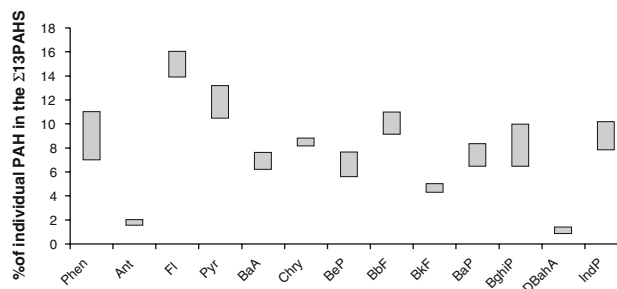


Fig. 7 Contribution of individual PAHs to the sum of 13 PAHs represented as a box covering media \pm standard deviation

Table 2 Range of PAHs in this work and other areas in the world

Area	Range (ng/g dry weight)	Reference
Ría de Vigo (Σ 13 PAHs)	29–3203	Present work
England and Wales (Σ 13 PAHs)	25–37110	Woodhead et al. (1999)
S. Francisco, California, USA (Σ 12 PAHs)	22–4400	Pereira et al. (1999)
Oaxaca, Mexico (Σ 11 PAHs)	10–2836	Botello et al. (1998)
Estuary in S. Carolina, USA (Σ 28 PAHs)	33–9600	Kucklick et al. (1997)
Mediterranean Sea (Σ 12 PAHs)	30–870	Baumard et al. (1998b)
Msan Bay, Korea (Σ 24 PAHs)	207–2670	Yim et al. (2005)

Table 3 Comparison of the sediments from the Ría de Vigo with the EAC values

		No. of PAHs > min EAC	Phen	Ant	Fl	Pyr	BaA	Chry	BaP
EAC min (µg/kg)			100	50	500	50	100	100	100
EAC max (µg/kg)			1000	500	5000	500	1000	1000	1000
Areas	Stations								
A	SR1	1				✓			
	SR2	3				✓		✓	✓
	SR3	3				✓		✓	✓
	SR4	5	✓			✓	✓	✓	✓
B	SR5	5	✓			✓	✓	✓	✓
	SR6	5	✓			✓	✓	✓	✓
	SR7	2				✓		✓	
	SR8	5	✓			✓	✓	✓	✓
	SR9	7	✓	✓	✓	✓	✓	✓	✓
C	SR10	5	✓			✓	✓	✓	✓
	SR11	5	✓			✓	✓	✓	✓
	SR12	5	✓			✓	✓	✓	✓
	SR13	1				✓			
	SR14	5	✓			✓	✓	✓	✓
	SR15	5	✓			✓	✓	✓	✓
	SR16	1				✓			
	SR17	0							
	SR18	1				✓			
D	SR19	4	✓			✓		✓	✓
	SR20	0							
	SR21	1				✓			
	SR22	0							
	SR23	0							
	SR24	0							
	SR25	0							
E	SR26	0							
	SR27	0							
	SR28	0							
	SR29	0							
F	SR30	0							
	SR31	0							
	SR32	0							
No. of stations > EAC min			11	1	1	19	10	14	13
% stations > EAC min			34	3	3	59	31	44	41

Note: ✓ = over EAC min;
 ✓✓ = over EAC max

Assessment Criteria (EAC) as established by OSPAR (OSPAR Commission 1997). EACs currently act as “guideline” assessment criteria and are not legislative in nature. No samples were found to exceed the maximum assigned EAC concentration. The minimum concentrations of the cited EACs are exceeded at some stations for some PAHs, ranging from 19 exceedences for pyrene (59% of the sampled stations) to only 1 for anthracene and fluoranthene (3%). A number of other stations primarily located in zones A, B, and C exceed the minimum EAC for a range of PAHs.

Quality guidelines as used in Canada (Smith et al. 1996) can also be used in the assessment of the quality of sediments with regard to the PAH concentrations. They establish two values: TEL (threshold effect level), the concentration under which adverse biological effects are rarely expected, and PEL (probable effect level), the concentration over which adverse biological effects are frequently expected. Concentrations falling between the PEL and TEL are expected to occasionally be associated with adverse biological effects.

Table 4 Comparison of the sediments from the Ría de Vigo with the TEL and PEL values

		No. of PAHs > TEL	No. of PAHs > PEL	Phen	Ant	Fl	Pyr	BaA	Chry	BaP	DBaH
TEL (ng g ⁻¹)				86.7	46.9	113	153	74.8	108	88.8	6.22
PEL (ng/g)				544	245	1494	1398	693	846	763	135
Areas	Station										
A	SR1	2	0			★					★
	SR2	4	0			★		★		★	★
	SR3	4	0			★		★		★	★
	SR4	7	0	★		★	★	★	★	★	★
B	SR5	8	0	★	★	★	★	★	★	★	★
	SR6	7	0	★		★	★	★	★	★	★
	SR7	5	0			★		★	★	★	★
	SR8	7	0	★		★	★	★	★	★	★
	SR9	8	0	★	★	★	★	★	★	★	★
C	SR10	7	0	★		★	★	★	★	★	★
	SR11	7	0	★		★	★	★	★	★	★
	SR12	7	0	★		★	★	★	★	★	★
	SR13	2	0			★					★
	SR14	7	0	★		★	★	★	★	★	★
	SR15	7	0	★		★	★	★	★	★	★
	SR16	2	0			★					★
	SR17	0	0								
SR18	1	0								★	
D	SR19	7	0	★		★	★	★	★	★	★
	SR20	0	0								
	SR21	1	0								★
	SR22	0	0								
	SR23	0	0								
	SR24	0	0								
	SR25	0	0								
E	SR26	0	0								
	SR27	0	0								
	SR28	0	0								
	SR29	0	0								
F	SR30	0	0								
	SR31	0	0								
	SR32	0	0								
No. of stations > TEL				11	2	17	11	14	12	14	19
% of stations > TEL				34	6	53	34	44	38	44	59

Note: ★ = over TEL;
★★ = over PEL

Polycyclic aromatic hydrocarbons concentrations in the sediments from the Ría de Vigo have been compared to these values (Table 4). Areas A, B, and C are clearly outlined and, in this case, it is possible to say that adverse biological effects might occasionally be expected in these areas due to PAH loadings.

Conclusions

The sediment samples collected in Ría de Vigo and its adjacent shelf present a clear PAH concentration gradient,

with higher values in the inner part of the estuary, especially near the city of Vigo and decreasing toward the outermost shelf area, where the lowest values were found.

Polycyclic aromatic hydrocarbons concentrations were found to be related to the particle size and the organic matter in the sediment, with, in general, higher PAH values in those sediments with smaller particle sizes (higher percentage of the <63- μ m fraction) and higher TOC content.

The PAH profile found is typical of pyrolytic origin as expected in an area mainly affected by urban and industrial inputs.

Sediments from the Ría de Vigo show comparable levels to those of similar estuaries. When compared to the EAC and TEL and PEL values, concentrations were found to be at low or medium levels, with only occasional biological effects as a result of PAHs expected to occur in zones A, B, and C.

References

- Baumard P, Budzinski H, Garrigues P (1998a) PAHs in Arcachon Bay, France: origin and biomonitoring with caged organisms. *Marine Pollut Bull* 36:577–586. doi:10.1016/S0025-326X(98)00014-9
- Baumard P, Budzinski H, Michon Q, Garrigues P, Burgeot T, Bellocq J (1998b) Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuary Coastal Shelf Sci* 47:77–90. doi:10.1006/ecss.1998.0337
- Baumard P, Budzinski H, Garrigues P, Dizer H, Hansen PD (1999) Polycyclic aromatic hydrocarbons in recent sediments and mussels (*Mytilus edulis*) from the Western Baltic Sea: occurrence, bioavailability and seasonal variations. *Marine Environ Res* 47:17–47. doi:10.1016/S0141-1136(98)00105-6
- Benner BAJ, Bryner NP, Wise SA, Mulholland GW, Lao RC, Fingas MF (1990) Polycyclic aromatic hydrocarbon emissions from the combustion of crude oil on water. *Environ Sci Technol* 24:1418–1427. doi:10.1021/es00079a018
- Botello AV, Villanueva SF, Diaz GG, Escobar-Briones E (1998) Polycyclic aromatic hydrocarbons in sediments from Salina Cruz Harbour and coastal areas, Oaxaca, Mexico. *Marine Pollut Bull* 36:554–558. doi:10.1016/S0025-326X(98)00026-5
- Cabanas López JM (1999) Temporal variability in the oceanographic conditions of the Galician offshore. Some biological consequences. PhD dissertation. University of Vigo, Spain
- Fraga F (1976) Fotosíntesis en la Ría de Vigo. *Inv Pesq* 40:151–167
- Franco MA, Viñas L, Soriano JA, Armas D, González JJ, Beiras R, Salas N, Bayona JM, Albaigé J (2006) Spatial distribution and ecotoxicity of petroleum hydrocarbons in sediments from the Galicia continental shelf (NW Spain) after the Prestige oil spill. *Marine Pollut Bull* 53:260–271. doi:10.1016/j.marpolbul.2005.10.004
- Kucklick JR, Sivertsen SK, Marion Sanders Scott GI (1997) Factors influencing polycyclic aromatic hydrocarbon distributions in South Carolina estuarine sediments. *J Exp Marine Biol Ecol* 213:13–29. doi:10.1016/S0022-0981(97)00007-5
- Law RJ, Biscaya JL (1994) Polycyclic aromatic hydrocarbons (PAH): problems and progress in sampling, analysis and interpretation. *Marine Pollut Bull* 29:235–241. doi:10.1016/0025-326X(94)90415-4
- Mariño Balsa JC, Pérez P, Estévez Blanco P, Saco Álvarez L, Fernández E, Beiras R (2003) Assessment of the toxicity of sediment and seawater polluted by the Prestige fuel spill using bioassays with clams (*Venerupis pullastra*, *Tappes decussatus* and *Venerupis rhomboideus*) and the microalga *Skeletonema costatum*. *Cienc Mar* 29:115–122
- Morales-Caselles C, Kalman J, Riba I, DelValls TA (2007) Comparing sediment quality in Spanish littoral areas affected by acute (Prestige, 2002) and chronic (Bay of Algeciras) oil spills. *Environ Pollut* 146:233–240. doi:10.1016/j.envpol.2006.04.042
- OSPAR Commission (1997) Agreed Ecotoxicological Assessment Criteria for metals, PCBS, PAHs, TBT and some organochlorine pesticides. Anex 6
- Pereira WE, Hostettler FD, Luoma SN, Av Geen, Fuller CC, Anima RJ (1999) Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. *Marine Chem* 64:99–113. doi:10.1016/S0304-4203(98)00087-5
- Salas N, Ortiz L, Gilcoto M et al (2006) Fingerprinting petroleum hydrocarbons in plankton and surface sediments during the spring and early summer blooms in the Galician coast (NW Spain) after the Prestige oil spill. *Marine Environ Res* 62:388–413. doi:10.1016/j.marenvres.2006.06.004
- Smith SL, MacDonald DD, Keenleyside KA, Gaudet CL (1996) The development and implementation of Canadian Sediment Quality Guidelines. In: Munavar M, Dave G (eds) Development and progress in sediment quality assessment: Rationale, challenges, techniques & strategies. SPB Academic Publishing, Amsterdam, pp 233–249
- Soclo HH, Garrigues P, Ewald M (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) Areas. *Marine Pollut Bull* 40:387–396. doi:10.1016/S0025-326X(99)00200-3
- Viñas L (2002) Evaluation of polycyclic aromatic hydrocarbons (PAHs) using HPLC in the Galician marine environment. PhD dissertation. University of Vigo, Spain
- Viñas L, Franco MA, González JJ (2002) Distribution of PAHs in surficial sediments of the Vigo estuary. Spain. Central axis and adjacent shelf. *Polycycl Aromat Comp* 22:161–173
- Webster L, Fryer R, Dalgarno EJ, Megginson C, Moffat CF (2001) The polycyclic aromatic hydrocarbon and geochemical biomarker composition of sediments from voes and coastal areas in the Shetland and Orkney Islands. *J Environ Monit* 3:591–601. doi:10.1039/b106408h
- Webster L, McIntosh AD, Moffat CF, Dalgarno EJ, Brown NA, Fryer R (2000) Analysis of sediments from Shetland Island voes for polycyclic aromatic hydrocarbons, steranes and triterpanes. *J Environ Monit* 2:29–38. doi:10.1039/a907556i
- Webster L, Twigg M, Megginson C, Walsham P, Packer G, Moffat CF (2003) Aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in sediments collected from the 110 mile hole and along a transect from 58°58.32'N 1°10.38'W to the inner Moray Firth, Scotland. *J Environ Monit* 5:395–403. doi:10.1039/b300633f
- Wise SA, Benner BA, Byrd GD, Chesler SN, Rebbert RE, Schantz MM (1988) Determination of polycyclic aromatic hydrocarbons in a coal tar Standard Reference Material. *Anal Chem* 60:887–894. doi:10.1021/ac00160a012
- Woodhead RJ, Law RJ, Matthiessen P (1999) Polycyclic aromatic hydrocarbons in surface sediments around England and Wales, and their possible biological significance. *Marine Pollut Bull* 38:773–790. doi:10.1016/S0025-326X(99)00039-9
- Yim UH, Hong SH, Shim WJ, Oh JR, Chang M (2005) Spatio-temporal distribution and characteristics of PAHs in sediments from Masan Bay. *Korean Marine Pollut Bull* 50:316–326. doi:10.1016/j.marpolbul.2004.11.003