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Sources, transport and fate of PAHs in sediments and superficial water of a chronically polluted semi-enclosed body of seawater: linking of compartments†

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This paper describes a study of the occurrence, levels and temporal evolution of PAHs in a bay characterized by persistent chronic impacts. A total of 40 samples, 20 of sediment and 20 of water, were taken at each of five different stations, in four sampling campaigns. Analyses of pollutants have been made using GC-MS. Results indicate that in a coastal environment subjected to chronic pollution by pyrolytic PAHs, episodes of petrogenic pollution, like oil-spills, can be identified by the combination of different source ratios. Results also indicate that, in the study area, PAHs are transported from superficial water to sediment. This conclusion is based on the degree of coincidence found in the presence/absence of individual PAHs in both compartments and in their petrogenic/pyrolytic nature, the positive sedimentation rate in the study area, together with the performance of the analyses of unfiltered water and the distribution of sources of PAHs found.

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Environmental impact

PAHs (polycyclic aromatic hydrocarbons) are ubiquitous pollutants in the environment, a few of them having well-known carcinogenic potential. Since the sources and abundance of PAHs are of special concern, these compounds have been studied in the two main abiotic marine compartments (sediment and seawater, compartments which may lead to exposure of aquatic organisms) of a semi-enclosed body of water, located between the Atlantic Ocean and the Mediterranean Sea and characterized by a chronic persistent impact. Occurrence, levels and temporal evolution of PAHs were studied. Results indicate that in a coastal environment subjected to chronic pollution by pyrolytic PAHs, episodes of petrogenic pollution, like oil-spills, can be identified by the combination of different source ratios. Results also indicate that in the study area PAHs are transported from superficial water to sediment.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of pollutants containing two or more fused benzene rings that are widely found in many environmental compartments. In coastal areas, anthropogenic PAHs enter the environment *via* run-off, industrial wastewaters and atmospheric emissions, vehicle exhaust gases, and spillage of fossil fuels. Concentrations of PAHs in seawater and sediments are of toxicological significance to both benthic and pelagic marine organisms.¹ The main sources of PAHs in the aquatic environment include the incomplete combustion of fossil fuels and other more recent organic matter (pyrolytic sources) at higher temperatures; the

slow maturation of organic matter under conditions of geochemical gradient (petrogenic sources); and short-term diagenetic degradation of biogenic precursors (diagenesis).^{2,3}

Because of their low solubility in water and hydrophobicity, PAHs in the marine environment rapidly become associated with organic and inorganic suspended particles,⁴ and subsequently they are deposited in sediments. As PAH solubility decreases with increasing molecular weight, organisms are often enriched in the lower molecular weight PAHs, relative to the sediment.^{5,6} This is because the heavier molecular weight compounds are preferentially adsorbed on sediment or associated with particulate matter while the lower molecular weight PAHs are dissolved slightly more than the heavier PAHs, although all of them are hydrophobic.⁷ Given these processes, it is necessary to measure the concentrations of these pollutants in water and sediment, to accurately monitor the condition of this part of the marine environment inhabited by many vulnerable species of living organisms.

General trends in PAH distribution in sediments can be observed between the two predominant sources: petrogenic and pyrogenic. Several indices are used to differentiate between pyrogenic and petrogenic sources; these include the ratio

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between low molecular weight (LPAHs) and high molecular weight (HPAHs) PAHs.⁸ LPAHs (\leq three rings) are produced abundantly at low to moderate temperatures, such as during petroleum and coal formation. In contrast, HPAHs (\geq four rings) are generated at high temperatures, such as in vehicle emissions and in biomass and coal combustion.^{9,10} Other frequently used indices are the phenanthrene/anthracene, fluoranthene/pyrene, and pyrene/benzo[*a*]pyrene ratios.¹¹

PAH levels found in marine sediments vary widely depending on geographical location. For example, PAH concentrations (the sum of 16 'priority' PAHs) as high as 48 000 ng g⁻¹ were found in Venice;¹² levels between 5700 and 8500 ng g⁻¹ were found in the Mediterranean littoral of France and Spain;⁷ and levels of approximately 800 ng g⁻¹ were found in Todos Santos Bay, Mexico.¹¹ Levels of PAHs in surface seawater vary widely, too. Witt¹³ found concentrations of up to 16 600 pg L⁻¹ in the Central Baltic Sea. In the Bahía Blanca estuary (Argentina), levels found ranged from 'undetected' to more than 4 μ g L⁻¹.¹ Concentrations (the sum of 15 'priority' PAHs) as high as 10 724 ng L⁻¹ were found in unfiltered water, in a study of seawater around England and Wales.¹⁴

Some of these PAHs are chemicals with known carcinogenic potential.¹⁵ For example, Giacalone *et al.*¹⁶ found that some PAHs can cause liver tumours in several species of fish and other aquatic organisms. Due to these properties and environmental implications, eight PAHs were included in the list of Priority Pollutants of the European Water Framework Directive¹⁷ and 16 in the United States Environmental Protection Agency (USEPA) Priority Pollutant List,¹⁸ 7 of them being potential carcinogens.

Because of these effects, the sources and abundance of PAHs are of special concern, and have been studied in the Bay of Algeciras (Spain). It is part of a unique and important coastal environment, located in South-western Europe, at the boundary between the Atlantic Ocean and the Mediterranean Sea. This Bay has long suffered chronic anthropogenic impact for several decades from urban and industrial sources. The Bay of Algeciras is an important industrial area of the Mediterranean Sea, with a large refinery (capable of processing twelve million tons of crude annually) and its associated petrochemical industry, in addition to steel, paper and power production (4 thermal power plants). Another significant source of pollution is the intense maritime traffic associated with the transportation of oil to and from the refinery, bunkering activities in the Bay and the commercial shipping activities of the Port of Algeciras, one of the largest in Europe and ranked among the most important ports of the world,¹⁹ which handled 43 million tons of goods in 2007.²⁰ Five large centres of population are located around the Bay: the City of Algeciras, Los Barrios, San Roque, La Línea de la Concepción, and Gibraltar. Together, these urban areas comprise more than 250 000 inhabitants (a population 'agglomeration' according to EU Directive 96/62/CE).²¹ The water of the Bay has a high rate of turnover because of its proximity to the Strait of Gibraltar and the strong currents that predominate in this area. This factor, together with its deep water, means that pollutants are dispersed in a large body of water and so their effects are considerably diminished.²²

Nevertheless, the anthropogenic effect on sediment and water quality in this Bay is considered a serious problem that must be studied.

The aim of this study is to characterize the pollution (sources, levels/quality and fate) and the transport of these pollutants between the compartments in a typical coastal geomorphologic unit (a semi-enclosed body of water) through the measurement and analysis of PAHs levels, in sediment and seawater from this coastal zone, and the connection between results in both compartments, studying the degree of coincidence in different comparisons.

Materials and methods

Sampling area

The Bay of Algeciras is located in the south of Spain, on the Strait of Gibraltar. The Bay is 9 km wide and 10 km long, covering an approximate surface area of 70 km², with a depth of up to 400 m in the centre of the Bay and 460 m in the mouth. It is delimited by Punta del Carnero (near the city of Algeciras) in the west and Punta Europa (Gibraltar) in the east (Fig. 1). The most external zones of the Bay present a greater movement of water, with a clearly decreasing trend towards the interior; however, as a result of the Bay's tidal current regime, water turnover is also relatively high in the area close to Gibraltar. The sedimentation rate is positive in all parts of the Bay, and it is

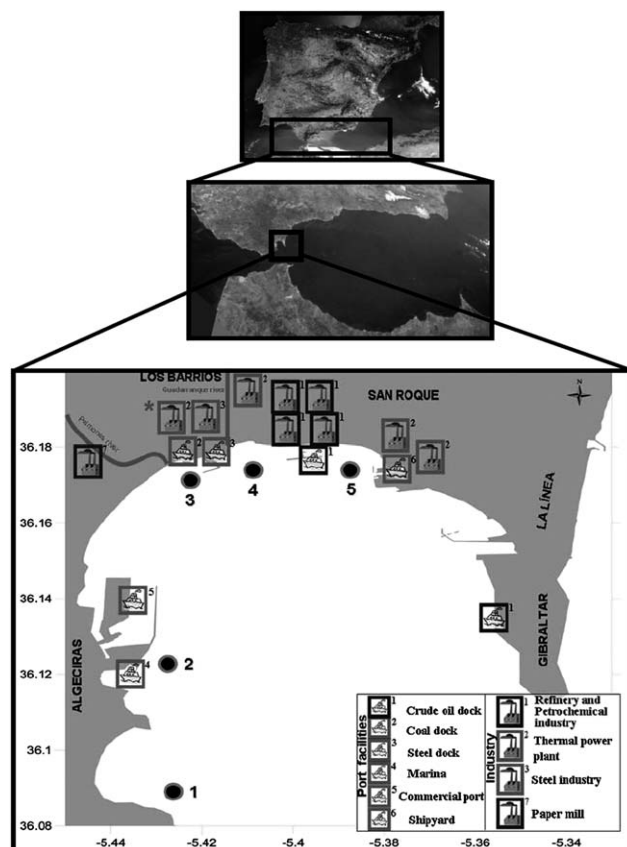


Fig. 1 Sampling area, showing the different sampling points and the most important industries and docks. *Coal electric power station.

generally higher in the innermost zones, especially those situated in areas influenced by the mouths of the rivers, being within 5 and 60 kg m⁻² per month at the sampling points of this study. The solids in suspension behave similarly, tending to increase towards the interior and with a marked effect due to proximity to river mouths and urban effluent discharge outlets.²³

In this study, five sampling points have been selected as representative zones of the Bay (Fig. 1), and four sampling campaigns were carried out at these points: “Getares”, relatively distant from potential sources of PAHs; “Isla Verde”, an area influenced by untreated urban waste-water; and “Palmones”, “Guadarranque” and “Puente Mayorga”, points close to industrial areas (a coal-fired power station, a steel processing plant, and a refinery – petrochemical complex, respectively).

Sample collection

Four sampling campaigns were carried out, in November '07 (SC1), May '08 (SC2), November '08 (SC3) and May '09 (SC4), and a total of 20 superficial sediment samples and 20 superficial water samples were collected at 5 locations (Fig. 1), being sampled quasi-simultaneously in the five points in all sampling campaigns. Sediment samples were obtained with a Van-Veen grab at depths ranging from 10 to 15 meters, and seawater was sampled with a stainless-steel recipient with amber glass bottles. From each location, approximately 400 g of sediment was placed in amber borosilicate containers with PTFE top and stored at -20 °C for subsequent analyses. Additionally, an extra 400 g was collected in plastic bags for purposes of sediment characterisation. Around 5 litres of water from each sampling point were kept at 4 °C before extraction in the laboratory within the following 24 h, in amber borosilicate bottles with PTFE top.

Analytical procedure for PAHs

In sediments, PAH analysis was based on the analytical procedure proposed by the USEPA.^{24,25} Approximately 2–4 g of sediment was weighed to an accuracy of 0.001 g and dehydrated with anhydrous Na₂SO₄. The samples were Soxhlet-extracted with 100 mL of dichloromethane–acetone (8 : 2 v/v) for 24 h (6 cycles per hour). The extracts were then purified on Florisil columns, and the PAHs were eluted with 100 mL of dichloromethane–hexane (2 : 8 v/v). The extract was concentrated to 1 mL using a rotary evaporator after changing the solvent from dichloromethane–hexane to acetonitrile. The Na₂SO₄ used was of analytical grade, and the dichloromethane, hexane, acetone and acetonitrile were of HPLC grade. A reference material (soil LGC6182) was analyzed, with 81–102% of certified values of PAHs obtained, except for benzo(*g,h,i*)perylene.

Average relative percent difference between triplicate (14%) was within acceptable limits, according to Levengood and Schaeffer.²⁶

In the case of water samples, the extraction was performed in a separator funnel without previously filtering the water. Volumes of 500 mL of water sample and 30 mL of hexane (HPLC grade) were shaken vigorously for about 7 min. Then, the hexane extract was separated and the aqueous phase was

re-extracted twice more with another 30 mL of hexane. This process was completed three times with three different aliquots of the same sample, and all the resulting extracts were combined. The extract was concentrated to 0.1 mL combining rotary evaporation and a gentle stream of nitrogen, after changing the solvent from hexane to acetonitrile (HPLC grade).

The concentration of 16 different PAHs was determined by gas chromatography-mass selective detection (GC-MSD) using a Voyager (ThermoElectron) gas chromatograph, according to Rojo-Nieto *et al.*²⁷ Briefly, the GC temperature program was: from 50 °C (1 min) to 120 °C (1 min) at 30 °C min⁻¹, and from 120 °C (1 min) to 260 °C (35 min) at 5 °C min⁻¹. The carrier gas was helium (flow rate 1 mL min⁻¹). The capillary column used was DB 1701 (J&W Scientific). The mass selective detector (MSD) was set to selective ion monitoring (SIM). Retention times and SIM were used for identification. The most abundant ion was used for identification and other ions were additionally used for confirmation. The detection limit in the extract was within 3 and 20 µg kg⁻¹, depending on the compound.

The temperature, salinity and dissolved oxygen of water were measured *in situ* with a portable electrochemical device. Suspended particulate matter (SPM) was quantified gravimetrically using 0.45 µm nylon filters (Osmonics, USA); and the concentrations of dissolved organic carbon were determined using a TOC analyser (Simadzu 5050A). Surface water samples for this analysis were collected using a peristaltic bomb (Masterflex 7521-00, poppet head 07518-10, Cole-Parmer Instrument Co., IL, USA), rigid Teflon pipes (FEP A-06450-07) and flexible Tygon tubing (6424-71). Water samples were picked up into LDPE bottles, which were pre-cleaned with 3 mol L⁻¹ HCl, rinsed with 10% HNO₃ and Milli-Q deionised water (Millipore, USA) six times, and stored in polyethylene bags until required.

Sediment characterisation

All the samples were dry-sieved in the laboratory using a Ro-Tap machine and seven sieves at 1 phi intervals; this procedure provided the statistical parameters described by Folk and Ward²⁸ for granulometry characterization. Following García-Robledo *et al.*,²⁹ organic matter was determined by loss on ignition. The carbon content was analysed using a LECO CHNS 932® analyser. The inorganic carbon content was quantified by analysing the carbon content in samples heated at 550 °C for 5 h. The organic fraction (TOC, total organic carbon) was determined as the difference in the carbon content between the initial dried and the heated samples.

Statistical analysis

The multivariate statistical technique used, principal component analysis (PCA), was carried out with the Statistica 6.0 (StatSoft®) software. Principal component analysis (PCA) allowed finding associations between variables, thus reducing the dimensionality of the data table. This is accomplished by diagonalization of the correlation matrix of the data, which transforms the “*n*” standardised original variables into “*n*” uncorrelated (orthogonal) ones (weighed linear combinations of the original variables) called principal components (PCs).

The eigenvalues of the PCs are the measure of their associated variance, the loadings indicate the participation of the original variables in the PCs, and the scores are the name given to the individual transformed observations. Data were standardized before analyses. A Varimax rotation allows the “cleaning up” of PCs by increasing the participation of the variables with higher contribution, and by simultaneously reducing that of the variables with lesser contribution. In that way, the number of original variables contributing to each VF is reduced at the cost of a loss of orthogonality. PCA inputs used were the not log-transformed variables, in original units.

Results and discussion

Occurrence, levels and quality

Tables 1 and S1† show the results obtained in the determination of the PAHs in water. It can be observed that the presence of each individual PAH in water samples is less, in line with the increasing molecular weight of the PAH (from the left to the right in Table S1†). This could be because the heavier the PAH, the lower its water solubility and the higher its octanol–water partition coefficient (K_{ow}).³⁰

With respect to the total concentration of all PAHs (TPAHs), no spatial or temporal pattern can be observed, except at sampling station 5 (Puente Mayorga) which was the least polluted station in all sampling campaigns (Table 1). This finding is despite this sampling point being the nearest to the probable major sources of PAHs (Fig. 1). One possible explanation of these results is the local hydrodynamics in this area.

Another important aspect studied is the abundance of high or low molecular weight PAHs (HPAHs and LPAHs) in water samples. As can be observed in Table 1, there is evidence of a

temporal evolution. In sampling campaigns 1 and 4, almost all sampling stations show higher concentrations of LPAHs, whereas in sampling campaigns 2 and 3 the most abundant PAHs are those of more than 4 rings (HPAHs). This temporal variation in the composition of total PAHs could indicate that a particular source of PAH was active in the period between campaigns 1 and 2, but ceased being active at some time between campaigns 3 and 4.

Two established water quality criteria for PAHs have been applied in the analysis of the results: the European Water Framework Directive, EWFD,¹⁷ and the Recommended Interim Marine Water Quality Criteria of British Columbia, RIMWQ.³¹ However, two points need to be taken into account in considering the analysis of the results. First, water samples were analysed without filtering, so the results include PAHs from particulate matter. This implies that results indicating values of PAHs lower than those of the guidelines can be considered of good quality, but also that results with values higher than the criteria do not necessarily imply bad quality. Secondly, whereas the RIMWQ quality guidelines refer to values at a specified point in time, the EWFD criteria refer mainly to annual mean values: values for the maximum allowable concentration at any point in time are proposed only for anthracene, fluoranthene and benzo(a)pyrene. In Table S1,† concentrations that exceed the quality criteria of RIMWQ and EWFD have been highlighted (shaded) and underlined respectively. In the EWFD criteria, in the case of the sum of benzo(b)fluoranthene plus benzo(k)fluoranthene and/or benzo(ghi)perylene plus indeno(1,2,3-cd)pyrene, samples 1 to 4 of SC2, 1 to 4 of SC3 and 4 of SC4 present concentrations exceeding the quality criteria in “annual mean values”. One sample (SC3P1) exceeds this guideline for a individual regulated PAH, benzo(a)pyrene, under the “maximum allowable concentration” criterion.

Table 1 Levels of PAHs ($\mu\text{g L}^{-1}$) in seawater: low molecular weight PAHs (LPAH), high molecular weight PAHs (HPAH), total PAHs (TPAH), pH, Dissolved Organic Carbon (DOC), dissolved oxygen (O_2), temperature (T), salinity (S) and Suspended Particulate Matter (SPM)

	LPAH	HPAH	TPAH	pH	DOC (mg L^{-1})	O_2 mg L^{-1}	T ($^{\circ}\text{C}$)	$S_{\text{‰}}$	SPM (g L^{-1})
SC1P1	0.1283	0.0242	0.1525	8.34	1.72	4.04	21.20	35.6	0.0270
SC1P2	0.2187	0.0225	0.2412	8.27	1.52	4.09	22.10	35.5	0.0240
SC1P3	0.1387	0.0020	0.1407	8.25	1.39	3.99	20.10	37.2	0.0240
SC1P4	0.1827	0.0207	0.2033	8.24	1.53	4.03	21.30	35.0	0.0320
SC1P5	0.0046	d.l. ^a	0.0046	7.03	6.23	4.08	21.00	34.4	0.0400
SC2P1	0.0487	0.1250	0.1737	8.42	0.41	6.55	18.30	34.8	0.0140
SC2P2	0.1030	0.1607	0.2637	8.42	0.59	7.03	19.70	33.9	0.0150
SC2P3	0.0554	0.0896	0.1451	8.56	0.67	6.85	20.20	32.4	0.0160
SC2P4	0.0642	0.0564	0.1206	8.51	0.72	6.94	20.90	33.8	0.0150
SC2P5	0.0395	0.0172	0.0567	8.58	0.56	6.85	18.90	33.5	0.0160
SC3P1	0.1158	1.2811	1.3969	7.98	1.74	5.68	14.90	32.9	0.0290
SC3P2	0.1067	0.7675	0.8742	8.03	1.03	5.44	15.90	32.8	0.0170
SC3P3	0.0480	0.2637	0.3116	8.06	0.66	4.67	15.40	32.2	0.0220
SC3P4	0.0283	0.1119	0.1402	8.04	1.67	5.27	15.30	31.2	0.0240
SC3P5	0.0050	0.0054	0.0104	8.07	1.52	4.58	14.30	32.4	0.0190
SC4P1	0.0401	0.0028	0.0429	7.11	0.92	7.50	18.20	30.1	0.0210
SC4P2	0.0889	0.0070	0.0959	6.96	2.51	7.20	18.30	29.3	0.0220
SC4P3	0.0817	0.0275	0.1092	7.58	0.41	7.90	18.20	30.3	0.0230
SC4P4	0.0540	0.1782	0.2322	7.37	1.05	7.47	18.60	29.5	0.0220
SC4P5	0.0378	0.0069	0.0448	7.42	1.14	7.72	18.50	29.7	0.0200

^a d.l. below determination limit.

In six samples benzo(a)pyrene exceeds the RIMWQ quality criteria for PAHs in seawater, although they do meet the EWFD standard (except for the mentioned previously). This difference could be because the RIMWQ criteria have been formulated to protect marine aquatic life from long-term effects (*i.e.* chronic toxicity) whereas the EWFD is more focused on acute toxicity. Most of the cases where levels exceed quality criteria are samples taken in campaigns 2 and 3. Considering that no significant differences were detected in particulate matter between campaigns (Table 1), and given the differences in LPAH – HPAH composition between campaigns 1–4 and 2 and 3, these results support the previously postulated explanation that a significant source of PAHs in the Bay was temporarily active between campaigns 1 and 4.

Table S2† presents the concentrations of individual PAHs found in sediments of the Bay. It can be observed that the least frequently found PAHs are benzo(ghi)perylene, dibenzo(ah)anthracene and indeno(1,2,3-cd)pyrene (*i.e.*, those with higher molecular weight). Nevertheless, unlike the findings in water samples, in sediments there is no evident pattern associated with the physical–chemical characteristics of PAHs and the frequency of individual compounds being present.

With respect to the concentrations of TPAH (Table 2), three groups of sediment samples can be distinguished: those with a TPAH concentration of less than 350 $\mu\text{g kg}^{-1}$ d.w. (seven samples); those with a TPAH concentration between 350 and 1000 $\mu\text{g kg}^{-1}$ (seven samples); and those with a TPAH concentration higher than 1000 $\mu\text{g kg}^{-1}$ d.w. (six samples). No clear temporal evolution of TPAHs has been observed in sediment samples, but in respect of their spatial distribution, it can be observed in Table 2 that, in the three last sampling

campaigns, station 1 presented TPAH concentrations lower than 350 $\mu\text{g kg}^{-1}$ d.w. The rest of the sampling stations present a high temporal variability with no common patterns.

In order to determine the degree of contamination by PAHs for sediments, three quality criteria have been considered: (1) the Dutch standards for contaminated sediments, $\Sigma 10\text{PAH } \mu\text{g g}^{-1}$ OC;³² (2) the consensus Sediment Quality Guidelines (SQGs) for total polycyclic aromatic hydrocarbons, $\Sigma 13\text{PAH } \mu\text{g g}^{-1}$ OC;³³ and (3) the criteria proposed by the National Oceanic and Atmospheric Administration.³⁴ According to the NOAA criteria, the ERL (Effects Range-Low) should be understood and used as an estimation of the concentration below which toxicity is improbable. Table S2† shows concentrations found that are above the ERL (highlighted) for the twelve PAHs considered in NOAA guidelines. As can be observed in Tables 2 and S2,† 11 of the 20 samples present between 2 and 5 concentrations of PAHs whose values lie between the ERL and the ERM (Effects Range-Median) criteria.

According to the Dutch standards ($\Sigma 10\text{PAH } \mu\text{g g}^{-1}$ OC), one sediment sample can be classified as heavily polluted (values above the level for which action is required); five samples are classified as polluted (values between the levels for which testing and action are required); thirteen samples as moderately polluted (values between the threshold value and that for which testing is required); finally, there is one sample that could be considered as slightly polluted or non-polluted (value below the threshold value). According to the consensus Sediment Quality Guidelines (SQGs) ($\Sigma 13\text{PAH } \mu\text{g g}^{-1}$ OC), fourteen sediments samples are below the TEC (Threshold Effect Concentration); five samples are between the TEC and MEC (Median Effect Concentration); one between the MEC and EEC (Extreme Effect

Table 2 Levels of PAHs ($\mu\text{g kg}^{-1}$ dry weight) in sediments: low molecular weight PAHs (LPAH), high molecular weight PAHs (HPAH), total PAHs (TPAH), Total Organic Carbon (TOC), and granulometry

	LPAH	HPAH	TPAH	TOC (%)	% >2 mm	% 2–0.063 mm	% <0.063 mm
SC1P1	587.80 ^a	554.20	1142.00	0.88	0.22	99.52	0.26
SC1P2	477.00	424.90	901.90	0.82	5.09	94.83	0.08
SC1P3	629.80 ^a	427.21	1057.01	1.94	1.11	85.31	13.58
SC1P4	475.90	260.00	735.90	2.03	4.35	88.74	6.91
SC1P5	371.60	192.20	563.80	0.77	24.03	75.09	0.88
SC2P1	147.50	42.42	189.92	0.06	0.33	99.45	0.22
SC2P2	573.10 ^a	917.60	1490.69	1.60	2.98	95.71	1.31
SC2P3	112.08	450.95	563.03	0.78	4.47	91.59	3.94
SC2P4	732.02 ^a	996.32	1728.34	0.20	2.05	96.3	1.65
SC2P5	94.90	40.29	135.20	0.09	1.4	96.1	2.5
SC3P1	221.45	54.11	275.56	0.08	2.31	77.98	0.71
SC3P2	774.57 ^a	1099.37	1873.94	1.04	6.9	92.98	0.12
SC3P3	110.49	57.18	167.67	1.51	0.06	92.35	7.59
SC3P4	379.23	241.40	620.64	1.73	0.28	96.14	3.58
SC3P5	272.84	726.58	999.43	0.68	0	95.42	4.58
SC4P1	10.14	12.96	23.10	1.77	1.58	98.04	0.38
SC4P2	26.07	41.28	67.35	0.50	10.23	88.1	1.67
SC4P3	19.69	52.38	72.08	0.51	0.05	90.01	9.94
SC4P4	444.26	988.53	1432.79	0.73	0.52	96.93	2.55
SC4P5	242.12	397.99	640.10	0.22	0	93.09	6.91

^a Concentration above ERL (NOAA).

Concentration); no sediments with concentrations above the EEC have been found in the Bay of Algeciras. If the Dutch and consensus SQGs quality criteria are compared it can be seen in Table 3 that a correspondence exists between these two sets of criteria. Thus, MECs in the SQGs seem to be equivalent to action values in the Dutch standards, and TECs in the SQGs seem to be related to test values in Dutch standards. The same correspondence has also been observed by Viguri *et al.*³⁵

To obtain a general overview of quality of sediments in the Bay of Algeciras, a numerical value has been assigned to each level of pollution considering these two sets of criteria together. In Table 3 a general temporal trend can be observed; initially (in sampling campaign 1) the Bay could be considered as moderately polluted by PAHs; six months later (in SC2), a pollution input event happened, because sediment quality has deteriorated, to the worst level of quality found in all four sampling campaigns. In sampling campaigns 3 and 4 the Bay sediment becomes slightly less badly polluted by PAHs. Nevertheless initial quality levels are still not reached one and a half years later. This evolution, similar to that observed in water, could indicate that a source of PAHs had been active in the period

between campaigns 1 and 2, and either finished or continued with less intensity, in the period between campaigns 3 and 4. In respect of the spatial distribution of sediment quality, results shown in Table 3 indicate that, in general terms, the area with the lowest sediment quality includes sampling points 4 and 5, while the less polluted zone comprises stations 1, 2 and 3.

Granulometry and total organic carbon (TOC)

Total organic carbon content and granulometry values found for sediment are also shown in Table 2. Seventeen of the twenty samples taken show a granulometry with more than 90% of grains between 2.000 and 0.063 mm in size (sand). The rest of the samples consist of two sediments with more than 10% of grains larger than 2 mm (coarse), and one (SC1P3) which has more than 10% of grains below 0.063 mm in size (silt). Comparing samples SC1P2 and SC1P3, both present similar values of TPAH concentration (Table 2), but SC1P3 has more than twice as much TOC content as SC1P2, and a higher content of fine sediments (<0.063 mm). On the other hand, SC2P3 and SC4P4 present very similar TOC contents as well as a similar fine fraction but their TPAH concentrations are very different. These two examples indicate that the properties of the sediment (fine fraction and TOC content) do not have a decisive influence on the final concentration of TPAHs. A similar absence of correlation has been observed in previous studies (Rojo-Nieto *et al.*, 2011). Levels of PAHs in sediments in this semi-enclosed body of water are more related to the spatial location, which is itself associated with major potential sources of PAHs.

Sources of PAHs

In order to determine whether the PAHs were from pyrolytic or petrogenic sources, three indicators were used: (1) the ratio between low and high molecular weight PAHs, (LPAH/HPAH);^{36,37} (2) the fluoranthene/(fluoranthene + pyrene) ratio;^{10,36} and (3) the anthracene/(anthracene + phenanthrene) ratio.^{10,36} They were chosen among the different ratios described to parental compounds since they were more applicable to all samples. According to Yunker *et al.*¹⁰ PAH ratio interpretations are most definitive for mass 202 (fluoranthene and pyrene) than for 178 (anthracene and phenanthrene), since the last one has much smaller energy differences between isomers and the ratio appears to be less responsive to differences in petroleum and combustion sources. It is also interesting to remark that fluoranthene–pyrene isomer pair degrades photolytically at comparable rates, suggesting that the original composition information is preserved during atmospheric transport. These ratios were also used in water because it is assumed that the PAHs present in these samples are strongly related to SPM (solid particulate matter), and these ratios are suitable to use in SPM.

Fig. 2 shows the most probable source of PAHs in each sampling campaign, according to these three criteria. In those cases where these ratios were contradictory, the sources were classified as “unidentified”. It can be observed that, in the majority of the samples, the sources of PAHs in water and sediments coincide (Fig. 2). No spatial evolution has been observed; in fact changes in sources of PAHs are more

Table 3 Sediment quality according to the Dutch standards for contaminated sediments (Kamer, 1994), to the consensus sediment quality guidelines for total polycyclic aromatic hydrocarbons (Swatz, 1999) and to the average of both criteria^a

KAMER	SC1	SC2	SC3	SC4	
P1	▲	◆	◆	●	5
P2	▲	▲	◆	▲	5
P3	▲	▲	▲	▲	3
P4	▲	■	▲	◆	7
P5	▲	◆	▲	◆	6
	5	9	7	6	
SWARTZ	SC1	SC2	SC3	SC4	
P1	▲	◆	◆	▲	6
P2	▲	▲	◆	▲	5
P3	▲	▲	▲	▲	4
P4	▲	■	▲	◆	7
P5	▲	◆	◆	◆	7
	4	9	8	7	
Average	SC1	SC2	SC3	SC4	
P1	1(2)	2	2	0.5	5.5
P2	1(2)	1	2	1	5
P3	1(2)	1	1	1	4
P4	1	3	1	2	7
P5	1	2	1.5	2	6.5
	5(8)	9	7.5	6.5	

^a ● = 0, below threshold value (Kamer, 1994); ▲ = 1, between threshold and test value (Kamer, 1994) and below TEC (Swartz, 1999); ◆ = 2, between test and action value (Kamer, 1994) and between TEC and MEC (Swartz, 1999); ■ = 3, above action value (Kamer, 1994) and between MEC and EEC (Swartz, 1999).

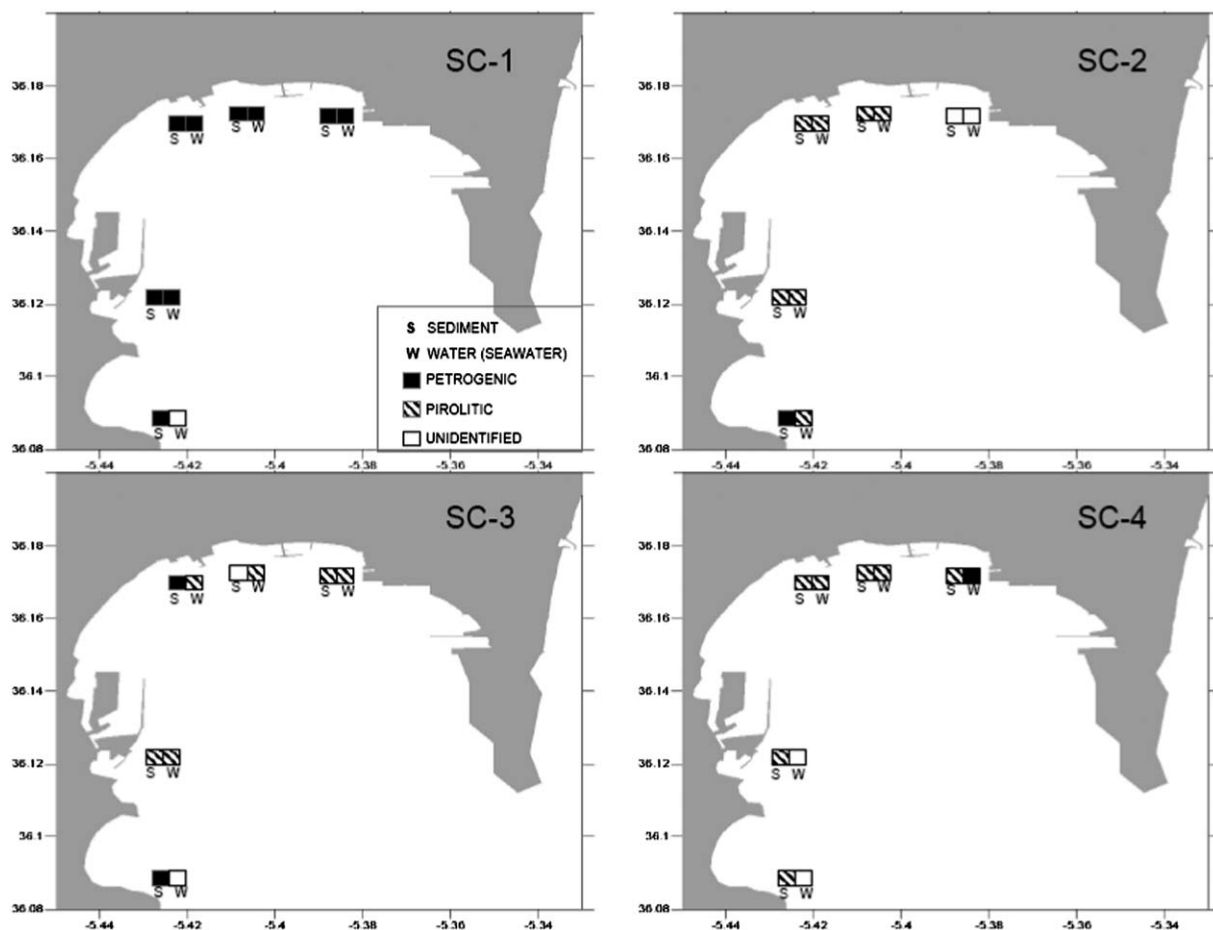


Fig. 2 Sources of polycyclic aromatic hydrocarbons of sediment and seawater in the sampling area, during the four sampling campaigns.

dependent on the sampling campaign than on the sampling location, probably due to rain periods, *etc.* Taking into consideration both sediment and water, an evolution from petrogenic to pyrolytic can be observed from SC1 to SC4 (Fig. 2). This change could be due to an accidental oil spill (the Sierra Nava accident) that had taken place on 28 January 2007, before the first sampling campaign. Therefore SC1 could be influenced by the last effects of this oil spill, whereas following campaigns show a gradual enrichment of pyrolytic PAHs. In a previous study²⁷ the concentration of PAHs in sediments was measured before and after the Sierra Nava accident. In this case, the source of PAHs changed from pyrolytic to petrogenic, which confirms that the accidental oil spill is the source of the petrogenic PAHs in sediments, and once the source stops, the PAHs change again to pyrolytic due to the persistent chronic input from industrial activities (Fig. 1). Fig. S1† represents the distribution of individual PAHs in sediments, where it can also be observed the evolution of individual compounds along the sampling campaigns, as in the case of sources.

By combining this conclusion on sources and the sediment quality results, an evolution can be observed, not only in sources but also changes in the spatial location of the more polluted areas, as well as the concentration of PAHs. Although in the first campaign all sampling stations showed the same

environmental quality (Table 3), the points with higher concentrations of TPAHs were 1, 2 and 3 (west coast), which were in the frontier of change of quality levels (showed in parentheses in the table), and the source in all sampling stations was petrogenic. These findings are consistent with the oil-spill accident previously mentioned being the major source, because the vessel Sierra Nava ran aground on Getares Beach, near to sampling point 1.

In the last sampling campaign, SC4, the most polluted zone was the north coast (points 4 and 5) and the source was pyrolytic. This is also consistent, because this is the area nearest to the chronic pyrolytic sources, the industrial area of the Bay. Sampling campaigns 2 and 3 are transition stages between the two extreme situations (1 and 4); they do not present a clear spatial distribution of PAH sources or concentration levels.

Statistical analysis

Principal Component Analysis (PCA) has been used to evaluate the results. Specifically, factorial analysis with extraction of principle components was performed to determine the principal variables that explain the majority of variance observed in the data. According to Liu *et al.*,³⁸ the factor loadings can be classified as “strong” “moderate” and “weak”, corresponding to

Table 4 Principal component analysis (PCA) of sediment samples. Factor loadings (varimax norm). Extraction: principal components^a

Variable	Factor 1	Factor 2	Factor 3
% >2 mm	*	*	*
% (0.063–2 mm)	*	*	*
% <0.063 mm	*	*	*
%TOC	*	*	*
Naphthalene	*		0.699133
Acenaphthylene	*	0.761122	*
Acenaphthene	*	0.753395	*
Fluorene	0.799838	*	*
Phenanthrene	0.593489	0.585303	*
Anthracene	*	0.778699	*
Fluoranthene	0.804515	*	*
Pyrene	0.788586	*	*
Benzo(a)anthracene	0.844406	*	*
Chrysene	0.794771	*	*
Benzo(b)fluoranthene	0.528354	*	*
Benzo(k)fluoranthene	*	0.676157	*
Benzo(a)pyrene	0.501186	0.795179	*
Benzo(g,h,i)perylene	0.522933	*	*
Dibenzo(a,h)anthracene	*	*	0.895432
Indeno(1,2,3-cd)pyrene	*	0.767770	*
Eigenvalue	7.217152	2.956917	2.091941
%Total variance	36.08576	14.78458	10.45971

^a *Below 0.5. Marked loadings are >0.70.

the absolute loading values of >0.70, 0.70–0.50 and 0.50–0.30 respectively. In the case of sediments, three principal factors explain more than 60% of cumulative total variance (Table 4). They are exclusively composed of different combinations of individual PAHs. This confirms the previous observation about the levels of PAHs in sediments being independent of granulometry or TOC values. However, in contrast to the results observed in previous studies (Rojo-Nieto *et al.*, 2011), in this case the main factors are less clearly related to LPAHs and/or HPAHs.

In the case of surface water, three principal factors explain more than 80% of cumulative total variance (Table 5). The first factor includes most of the individual PAHs. The second factor comprises certain physical–chemical characteristics of the water; and the third factor includes three PAHs of low molecular weight (naphthalene, acenaphthene and fluorene). The behaviour of PAHs in water is strongly influenced by both the individual PAHs and their molecular weights (factors one and three) and the physical–chemical characteristics of the medium (factor two). The three groups obtained (LPAHs, HPAHs and physical–chemical characteristics) can be observed in Fig. 3.

In the case of the influence of the nature of the PAHs, this has been previously commented in the section on “Occurrence, levels and quality”. The physical–chemical characteristics of the matrix have a great influence on the distribution of PAHs in seawater: in this case, factor 2 comprises salinity and suspended solids, among other variables. Compounds of heavier molecular weight preferentially associate with suspended particles while the PAHs of lower molecular weight are preferentially dissolved (Baumard *et al.*, 1999). In the case of salinity,

Table 5 Principal component analysis (PCA) of seawater samples. Factor loadings (varimax norm). Extraction: principal components^a

Variable	Factor 1	Factor 2	Factor 3
DOC (mg L ⁻¹)	*	0.667327	*
O ₂ (mg L ⁻¹)	*	–0.883667	*
T ^o (°C)	–0.55584	*	0.519991
Salinity‰	*	0.744171	*
SPM (mg L ⁻¹)	*	0.718097	*
Naphthalene	*	*	0.879693
Acenaphthylene	*	*	*
Acenaphthene	*	*	0.722381
Fluorene	*	*	0.800868
Phenanthrene	0.87759	*	*
Anthracene	0.92665	*	*
Fluoranthene	0.92821	*	*
Pyrene	0.90397	*	*
Benzo(a)anthracene	0.99498	*	*
Chrysene	0.98994	*	*
Benzo(b)fluoranthene	0.98883	*	*
Benzo(k)fluoranthene	0.98934	*	*
Benzo(a)pyrene	0.98918	*	*
Benzo(g,h,i)perylene	0.97125	*	*
Dibenzo(a,h)anthracene	0.88569	*	*
Indeno(1,2,3-cd)pyrene	0.98535	*	*
Eigenvalue	11.70920	2.86802	2.18390
%Total variance	55.75808	13.65726	10.39952

^a *Below 0.5. Marked loadings are >0.700000.

the solubility of PAHs is influenced through the salting-out effect.

The most important factor (factor 1) comprises mainly HPAHs. The strong presence of these PAHs found in water samples is because the analyses were performed on unfiltered water; in other words, the water contained suspended particulate matter (SPM) to which HPAHs were associated.

Presence/absence of PAHs in sediments and water

A comparison has been made between water and sediment samples from the same sampling point in the same sampling campaign, in respect of the particular individual PAHs that are present or absent in each. In 65% of the cases there is coincidence on the presence or absence of individual PAHs in both water and sediments, in samples from the same place at the same time. This coincidence, together with the fact that water was analyzed unfiltered, indicates that PAHs in SPM and in sediments could have the same source. Moreover, the sedimentation rate is positive in coastal areas of the Bay of Algeciras, being within 5 and 60 kg m⁻² per month at the sampling points of this study, and resuspension from the sediment does not reach the superficial water in the study area in depths of 10–15 m, so SPM is deposited on sediments in these littoral areas. All these findings constitute evidence that, in the Bay of Algeciras, PAHs are transported from superficial waters to sediment, through SPM deposition. The sources of PAHs in superficial seawater in this study area are, mainly, atmospheric deposition (pyrolytic source) as a persistent chronic source, and, in specific cases, oil-spill accidents (petrogenic source).

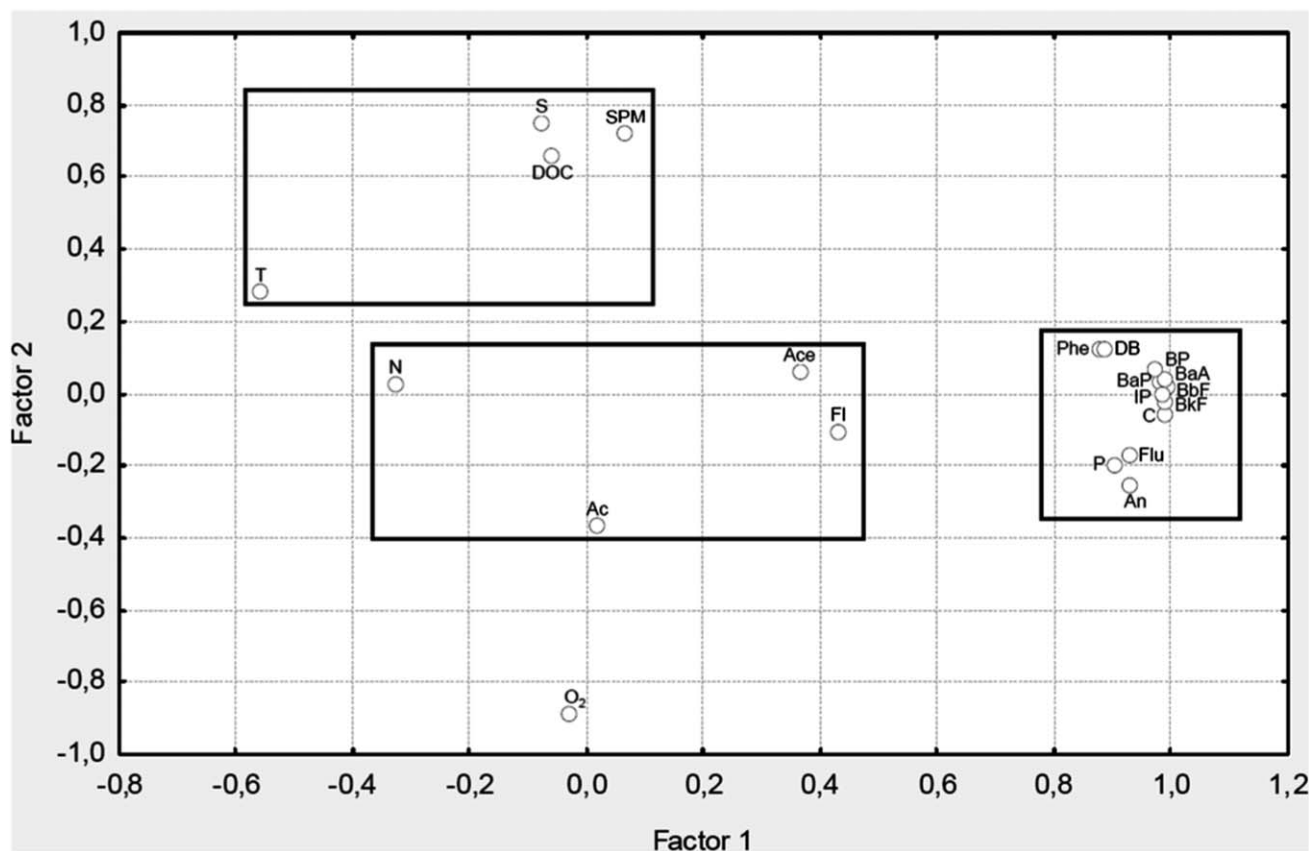


Fig. 3 Scores of variables studied in seawater, on the plane defined by the first two principal components. N: naphthalene, AC: acenaphthylene, Ace: acenaphthene, FI: fluorene, Phe: phenanthrene, An: anthracene, Flu: fluoranthene, P: pyrene, BaA: benzo(a)anthracene, C: chrysene, BbF: benzo(b)fluoranthene, BkF: benzo(k)fluoranthene, BaP: benzo(a)pyrene, BP: benzo(ghi)perylene, DB: dibenzo(a)anthracene, IP: indeno(1,2,3-cd)pyrene, DOC: dissolved organic carbon, S: salinity, T: temperature, SPM: suspended particulate matter and O₂: dissolved oxygen.

Conclusions

Despite the study area being a semi-enclosed Bay with high water circulation, and hence with high dilution capacity, the spatial distribution of PAHs in the sediment is related more closely to the location, with respect to the potential sources of these pollutants, than to substrate properties such as the content of fine fraction grains or the TOC. The physical and chemical properties of PAHs (solubility, K_{ow}), and of the matrix (salinity, SPM content) are a determining factor in the distribution observed in the aquatic compartment. In a coastal environment subjected to chronic pollution by pyrolytic PAHs, the use of the LPAHs/HPAHs, fluoranthene/(fluoranthene + pyrene) and anthracene/(anthracene + phenanthrene) ratios in combination is useful in identifying specific petrogenic pollution episodes, like an oil-spill. The Dutch ($\Sigma 10\text{PAH } \mu\text{g g}^{-1} \text{OC}$) and consensus SQGs ($\Sigma 13\text{PAH } \mu\text{g g}^{-1} \text{OC}$) quality criteria for establishing the degree of contamination of sediments by PAHs are comparable, so the proposed combined use of both is useful for determining the environmental quality of sediments and their evolution, the environmental quality of them being slightly to heavily polluted by PAHs. Considering: (a) the degree of coincidence found in the presence/absence of individual PAHs in water and sediment, as well as the petrogenic/pyrolytic

nature; (b) that the analysis of PAHs in water samples was performed on unfiltered matrices; (c) the positive sedimentation rate in coastal areas of the Bay of Algeciras; and (d) the sources of PAHs in the studied area, with high potential for inputs of PAHs *via* atmospheric deposition, the results of this study indicate that there is transport of PAHs from superficial waters to sediment, through SPM deposition.

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