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# Polycyclic aromatic hydrocarbons in surface sediments of the mid-Adriatic and along the Croatian coast: Levels, distributions and sources<sup>☆</sup>

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## ABSTRACT

This study provides contamination levels, distributions and source apportionment of PAHs in surface sediments in the mid-Adriatic and along the Croatian coast. Median summed concentrations of parent and alkyl-PAHs are circa 10 times lower in the off-shore transect stations of the mid-Adriatic (22.3 and 18.2  $\mu\text{g}\cdot\text{kg}^{-1}$  d.w.) than the ranges determined at the coastal stations, including those of Kaštela bay (227–331 and 11.7–197  $\mu\text{g}\cdot\text{kg}^{-1}$  d.w., respectively). The highest levels, circa 20 times higher, were found in Šibenik bay (median 6603 and 3051  $\mu\text{g}\cdot\text{kg}^{-1}$ ). The overall range of PAH concentrations spans more than 2000 times between the lowest and the highest contamination level. The geographical distributions reflect the presence of strong gradients at local and regional scales. A major factor influencing sedimentary PAH distributions at local scale appears to be the distance from their known continental and coastal upstream emission sites (urban, industrial, harbour ...), whereas at regional scale, this distribution depends more on the routes of entry of PAHs into the study area. Two combustion and one petroleum model source profiles of PAHs were determined by alternative least square analysis. Benzo[*b*+*j*] fluoranthenes and fluoranthene/pyrene are compounds characterizing two pyrogenic sources respectively, while signatures of alkyl-substituted homologues (phenanthrenes/anthracenes, fluranthenes/pyrenes, chrysenes and dibenzothiophenes) delineate a petrogenic source profile. The quantitative apportionment of source contributions shows significant geographical differences, with a dominant petrogenic source found along the mid-Adriatic transect (approximately 74%) and in Kaštela bay (61%). In the coastal sediments about a fifty-fifty contamination mix is assigned to a petrogenic/pyrogenic source of PAHs (47% and 53% respectively), whereas in Šibenik bay a strong predominance is apportioned to the combustion compounds (81%).

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widespread organic pollutants in current marine and terrestrial environments (Laflamme and Hites, 1978). Although certain of these hydrocarbons also have natural origins, anthropogenic PAHs predominate in today's environments (Neff, 1979; Venkatesan, 1988; Wakeham et al., 1980). A large number of anthropogenic PAHs are recognized as strong mutagens and carcinogens (Allen et al., 1998; Durant et al., 1998), representing a significant public

health concern and threats to ecosystems. Actually, PAHs are on the lists of priority pollutants and substances in the USA and Europe, aiming at better control, regulation and the reduction of water and air pollution by these chemicals (EPA, 2014; EU, 2013). The effective mitigation and remediation measures of this pollution require an understanding of the various sources of PAH contributions found in a specific region. In the marine environment, the major sources of anthropogenic PAHs are related to releases of crude petroleum and its numerous derivatives and to all inputs of compounds derived from the incomplete combustion of biomass and fossil- and modern bio-fuels (Fraser et al., 1998; Dachs et al., 2002; Deyme et al., 2011). The pathways of petroleum-derived PAHs are mainly regular spillages from various maritime activities (transport, oil exploitation, harbour operations ...) as well as accidental oil spills,

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whereas combustion-derived PAHs (generally from marine and continental transport, power and heat plants, residential warming and specific industries) enter the marine environment mainly via the atmospheric fallout of soot particles and continental watershed runoff, including, direct discharges of storm waters from coastal large coastal cities and industrialised sites (Lima et al., 2005; Guo et al., 2007; Gonul and Kucuksezgin, 2012). Due to strong sorption propensity, many environmental PAHs are associated with particles (Karickhoff et al., 1979; Dachs et al., 2002; Zhao et al., 2013). Despite their long-range global atmospheric transport (Fernandez et al., 2000; EEA, 2013), PAHs are also deposited in large amounts in coastal sediments, showing a strong decline of their concentrations with increasing distance from the coast (Lipiatou et al., 1997; Tsapakis et al., 2003; Cathalot et al., 2013).

In this context, complementary and alternative approaches for the characterization of PAH sources are continuously developed. Common emissions and discharge inventory studies have provided emerging regional and local trends, and a generally good correspondence between emissions of PAHs and records of energy production and fossil-fuels consumption (Zhang and Tao, 2009; EEA, 2013; Shen et al., 2013). However, highly variable emission factors have been reported, thus indicating great uncertainties in the environmental inventories of PAHs (Jenkins et al., 1996; Pacyna et al., 2003; Johansson et al., 2004; Lee et al., 2005; Chen et al., 2005). Many reported studies are based on the understanding of spatial distributions and the identification of point emission sources, the interpretations of compositional molecular signature fingerprints and diagnostic source ratios of specific PAHs determined in diverse receptor compartments, namely, the atmosphere, sediments, biota (Douglas et al., 1996; Yunker et al., 2002; Neff, 2002; Christensen et al., 2004; Zhang et al., 2005). More recently, chemometric analyses have also been applied for PAH source characterization (Larsen and Baker, 2003; Li et al., 2003; Comero et al., 2009; Stout and Graan, 2010). This approach is often referred to as the source apportionment method, allowing the determination of a number of contributing sources as chemical profiles (“end-member” signature fingerprints) and the relative amounts of each source present in a sample. For instance, in the urban atmosphere of Baltimore, based on multivariate statistics and receptor environment models, such methods allowed the resolution and apportionment of up to six combustion sources of PAH (Larsen and Baker, 2003). Finally, the radiocarbon analysis of individual PAH compounds in different sedimentary and atmospheric environments was also used as the most reliable method to determine the relative contributions of fossil fuel and biomass combustion sources of PAHs (Mcare et al., 2000; Reddy et al., 2002; Mandalakis et al., 2004, 2005; White et al., 2005; Kumata et al., 2006; Cathalot et al., 2013). Such determinations, using PAHs as excellent molecular tracers of combustion particles, may also contribute to more fundamental assessments of pyrogenic/combustion carbon contributions to various pools of organic carbon budgets, and therefore are carried out as well in the context of global climate change studies (White et al., 2005; Dickens et al., 2004). However, this later method is very demanding and reserved for specialized laboratories.

In this study, we report on PAH levels, distributions and source characterization determined in the surface sediment of the mid-Adriatic and along the Croatian coast. Extensive analyses of PAHs in the sediment samples included unsubstituted parent compounds, alkyl-substituted homologues and sulphur heterocyclic compounds. Four zones were studied: the mid-Adriatic transect, a coastal survey from the north-west to the south-east along the Croatian shoreline and two urban-industrial zones: Šibenik and Kaštela bays. This regional/local geographical coverage was arranged so that it included known and suspected

contaminant emission sites and reference sites away from direct pollution sources. Finally, PAH source characterization in this study is based on the wide range of analyzed compounds, together with geographical distribution data it also includes an examination of carefully selected meaningful source-specific diagnostic ratios and correlations, explanatory multivariate statistics by principal component (PCA) and hierarchical cluster (HCA) analyses, and chemometrics receptor environment analysis using the alternative least square (ALS) calculation method. The results include the identification of PAH chemical source profiles and the quantification of the relative contributions of these sources in the studied areas. Consequently the results presented provide a coherent set of reference data on the contamination of marine sediment by PAHs in the mid-Adriatic and along the Croatian coast.

## 2. Materials and methods

### 2.1. Sample collection and pre-treatment

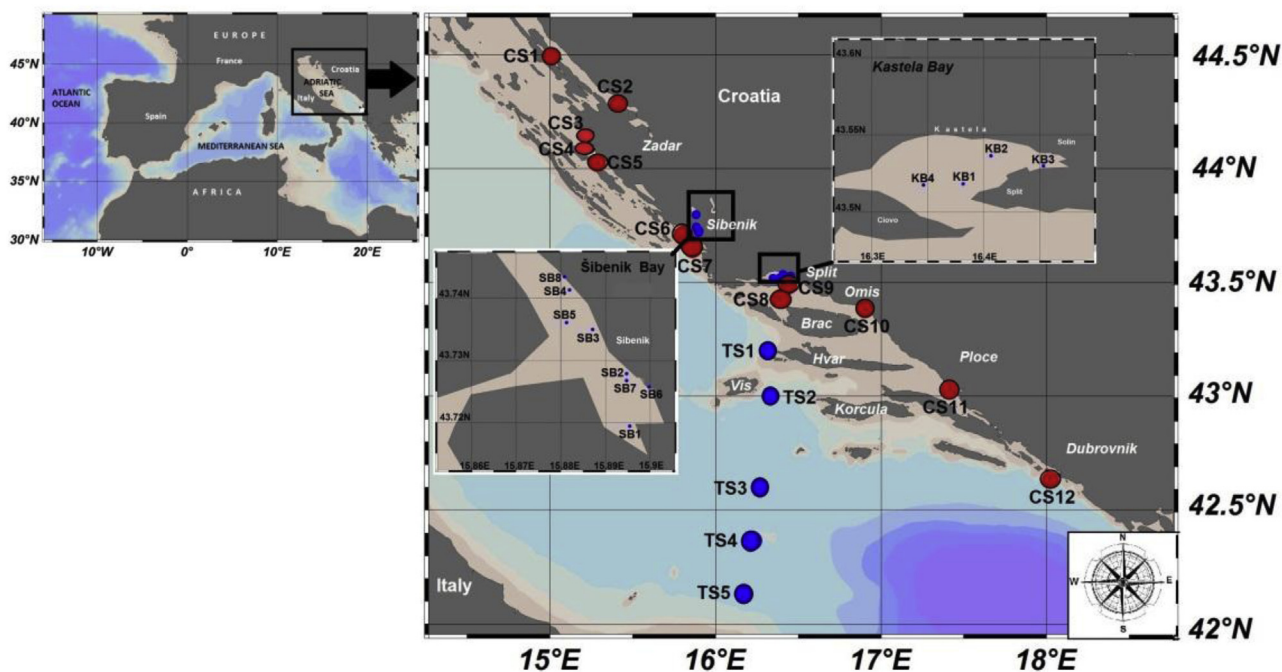
Sediment samples were collected from the *R/V Bios 2* (IOF/Croatia) during three campaigns in 2013. In total, 29 stations were sampled in the four studied areas: the mid-Adriatic transect, a coastal survey from north-west to south-east along the Croatian shoreline (from 44.49005 N and 15.01010 E to 42.63339 N and 18.02187 E) and two urban-industrial sites, Šibenik and Kaštela bays (Fig. 1, Table S-1 and S-2). Approximately, 200 g of wet surface sediment were manually subsampled using stainless steel spatula from the centre of Van Veen Grab. The grab sampling may roughly represent 0.1 m<sup>2</sup> of surface sediment. The sediment sub-samples were wrapped in pre-cleaned aluminium foil and subsequently frozen on-board at –20 °C. Samples were transferred frozen to the laboratory, freeze-dried and subsampled for the chemical and sediment characterization analysis. The sediment aliquots for PAH analyses, were further sieved through a 2 mm stainless steel screen and stored in pre-cleaned glass jars until laboratory analyses.

### 2.2. Grain size distribution

A weighted sample aliquot of dry granular sediment is processed through a nested set of standardized sieves with progressively smaller openings of: 4, 2, 1, 0.5, 0.25, 0.125 and 0.063 mm. The smaller than 0.063 mm sediment fraction was determined by the aerometric method according to Casagrande (Ostrowska et al., 1991). The fractions were described according to Wentworth Grade Scale (1922): gravel-sized particles have a nominal diameter of 2 mm; sand-sized particles have nominal diameters of <2 mm to >63 μm; silt-sized particles have nominal diameters of <62.5 μm to >4 μm; and clay is <4 μm. The parameters calculated for grain size include: mean, median, sorting and skewness (Table S-2).

### 2.3. Organic matter determination

The amount of organic matter was determined by gravimetric measurements as lost by ignition at 450 °C. Approximately 0.5 g of a dried, ground and sieved (4 mm) sediment sample aliquot is weighted precisely in a crucible. Crucibles are then dried at 110 °C for 24 h. When cooled, the crucibles are reweighed and treated with 30% H<sub>2</sub>O<sub>2</sub>. Once the samples have been dried, the crucibles are placed in a furnace and ignited at 450 °C for six hours.



**Fig. 1.** Map showing positions of the surface sediment sampling stations in four study areas: the mid-Adriatic transect, a coastal survey north-west – south-east, Šibenik and Kaštela bays.

#### 2.4. PAH analysis

The analytical method is described in more detail elsewhere (Tronczyński et al., 2004). Briefly, the analysis of PAHs in the surface sediment included different groups of unsubstituted parent compounds (PAH), alkyl-substituted homologues (C-PAH) and both unsubstituted and alkyl-substituted polycyclic aromatic sulphur heterocyclic compounds (SPA and C-SPA). The concentrations were determined for individual compounds and for their alkyl-substituted homologue groups (Table S-3). Aliquots of dry sediments (5–20 g) of each sample were extracted twice using dichloromethane by accelerated solvent extraction (Dionex ASE 200). Prior to extraction, sediment samples were spiked with perdeuterated recovery standards (phenanthrene- $d_{10}$ , benzo[e]pyrene- $d_{12}$  fully deuterium labelled compounds). The organic extracts were concentrated using rotary evaporation and nitrogen gas and then purified and fractionated by a two-layer 5% deactivated silica/alumina column. The PAHs were analyzed and quantified by gas chromatography coupled to the mass selective detectors (GC-MS Agilent Technologies models 7890/5975). Prior to GC-MS analysis, all sample extracts and calibration solutions in auto-sampler vials were quantitatively spiked using a robotic auto-sampler with an internal standard mixture containing deuterated compounds: acenaphthene- $d_{10}$ , fluorene- $d_{10}$ , pyrene- $d_{10}$ , benz[a]anthracene- $d_{12}$  and indeno[1,2,3-cd]pyrene- $d_{12}$ . The quantification of individual PAH compounds and group of their alkyl-homologues in the samples was carried out by using corrected response of GC-MS with the response of correspondent surrogate quantification standard. The replicate analysis of EC-2 NWRI (Environment Canada) sediment samples of certified reference material for PAHs was used for the assessment of the precision and accuracy of the entire analytical protocol. The accuracy was between 60 and 93% of certified values ( $n=6$ ) and relative standard deviation of repeated analysis was better than  $\pm 16\%$  for all quantified PAH analytes in the sediment samples. Average recovery of standards (phenanthrene- $d_{10}$  and benzo[e]pyrene- $d_{12}$ )

was  $73 \pm 16\%$  while samples with low recovery ( $<50\%$ ) were excluded.

#### 2.5. Statistics

Hierarchical cluster (HCA) and principal component analysis (PCA) of PAH data were performed using Pirouette multivariate data analysis software (Infometrix, 2014). For both analyses the PAH concentration data were pre-processed by autoscaling, i.e. mean-centering followed by variance scaling. For HCA we used Euclidean distance between samples, expressed on the standard scale of similarity where a value of 1 is assigned to identical samples and a value of 0 to the most dissimilar samples. The samples were clustered by the incremental link method used to calculate inter-cluster distances (i.e. a sum of squares approach). For PCA, total variability of the original PAH data is represented by a minimum number of factors with a subsequent varimax (normal) rotation of factors, which maximizes the variance of the loadings by sequentially rotating PCA loadings pair-wise. Finally, in the receptor model, the problem is considered as a solution of the chemical mass balance equation in a number of source profiles, and their contributions to each individual sample. The number of sources is related to total variance, where the alternating least square (ALS) calculation requires an iterative technique to obtain the most meaningful solution, that is, the best fitting compositions and profiles (Tauler et al., 1993). The algorithm used in the present estimates, is based on “convexity” calculation (Grande and Manne, 2000), it finds the purest “shapes” in the original PAH concentration data, determining row-wise estimates of profiles, and column-wise estimates of composition (Pirouette, Infometrix, 2014). The source profiles are interpreted as source types (combustion/pyrogenic and petroleum/petrogenic), also using known emission/discharge information and geographical distribution results.



### 3. Results and discussion

#### 3.1. Levels, spatial distributions and gradients

Concentrations of main suites of PAH determined in the sediments of four studied areas (mid-Adriatic transect, coastal transect, Kaštela and Šibenik bays) are summarized in Table 1 and further detailed in SI (Fig. S-1 and Table S-4). The summed concentrations of parent and alkyl-PAH ranged from 8.50 to 18348  $\mu\text{g kg}^{-1}$  and from 2.95 to 5770  $\mu\text{g kg}^{-1}$  dry weights, respectively. Levels of parent and alkylated sulphur heterocyclic PAHs ( $\Sigma\text{S-PAH}$ ,  $\Sigma\text{CS-PAH}$ ) were within the ranges 0.336–514  $\mu\text{g kg}^{-1}$  and 0.292–977  $\mu\text{g kg}^{-1}$  d.w., respectively.

The lowest concentrations of summed total PAHs ( $\Sigma\text{T-PAH}$ ), were determined along the mid-Adriatic transect ( $\Sigma\text{T-PAH}$ , range 11.7–282  $\mu\text{g kg}^{-1}$ , d.w.), the intermediate levels were determined in the coastal and Kaštela bay sediments ( $\Sigma\text{T-PAH}$ , range 117–2580  $\mu\text{g kg}^{-1}$ , d.w.) and the highest level of contamination by PAHs was found in Šibenik bay ( $\Sigma\text{T-PAH}$ , range 6610–24576  $\mu\text{g kg}^{-1}$ , d.w.). The very low concentrations determined along the transect (especially at off-shore stations TS1 and TS2) correspond to PAH levels reported in sediments from open sea areas in the eastern Mediterranean and Cretan Sea (Lipiatou et al., 1997; Tsapakis et al., 2003; Gogou et al., 2000; Gonul and Kucuksezgin, 2012) and also from remote locations of the world oceans, such as the Barents Sea (Savinov et al., 2003) and arctic lakes (Fernandez et al., 2000). These levels remain within the range of background reference concentrations of PAH in marine sediments (Ospar/Ices, 2004; Azoury et al., 2013; UNEP, 2016). Interestingly, higher concentrations along the mid-Adriatic transect were found at stations TS3 and TS5. The concentrations increase systematically from TS1 to TS3 probably indicating a local concentration gradient in this area. TS3 is located along the route of the densest maritime traffic in the Adriatic (Morović et al., 2015).

**Table 1**  
Summed concentration of PAHs ( $\mu\text{g kg}^{-1}$  dry weight) in the surface sediments of the offshore mid-Adriatic and along the Croatian coast.

Zone		Min	1stQu.	Median	3rdQu.	Max	Average	N
<b>Transect</b>	$\Sigma\text{PAH}$	8.50	9.04	17.34	45.34	117.2	34.16	9
	$\Sigma\text{C-PAH}$	2.95	4.32	8.07	34.39	135.4	31.08	9
	$\Sigma\text{S-PAH}$	0.336	0.465	0.782	1.87	4.20	1.38	9
	$\Sigma\text{CS-PAH}$	0.292	1.16	2.06	3.46	13.27	3.49	9
<b>Coast</b>	$\Sigma\text{PAH}$	81.24	124.4	148.7	357.1	1705	395.5	12
	$\Sigma\text{C-PAH}$	31.09	46.80	109.7	254.5	831.7	227.0	12
	$\Sigma\text{S-PAH}$	3.03	4.99	6.707	17.38	64.96	15.68	12
	$\Sigma\text{CS-PAH}$	1.76	7.77	18.36	44.02	157.5	42.25	12
<b>Kaštela</b>	$\Sigma\text{PAH}$	114.4	134.6	330.9	521.9	1114	399.0	9
	$\Sigma\text{C-PAH}$	17.68	82.52	197.1	440.2	936.9	327.0	9
	$\Sigma\text{S-PAH}$	2.23	12.11	15.25	42.76	59.9	26.3	9
	$\Sigma\text{CS-PAH}$	2.40	27.75	49.93	161.8	331.6	107.7	9
<b>Šibenik</b>	$\Sigma\text{PAH}$	4629	6049	6603	13018	18348	9614	17
	$\Sigma\text{C-PAH}$	1290	2456	3051	4892	5770	3416	17
	$\Sigma\text{S-PAH}$	101.7	232.8	265.8	310.2	514.0	286.6	17
	$\Sigma\text{CS-PAH}$	119.3	174.4	230.4	382.9	976.7	327.3	17

$\Sigma\text{ PAH}$ : Sum of unsubstituted compounds phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene + triphenylene, benzo[b]fluoranthene + benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene, benzo[ghi]perylene.

$\Sigma\text{ C-PAH}$ : Sum of alkyl-phenanthrenes/anthracenes, alkyl-fluoranthenes/pyrenes, alkyl-chrysenes, alkyl-benzofluoranthenes.

$\Sigma\text{ S-PAH}$ : Sum of unsubstituted dibenzothiophene and three isomers of benzonaphthothiophenes.

$\Sigma\text{ CS-PAH}$ : Sum of alkyl-substituted dibenzothiophenes and benzonaphthothiophenes.

Furthermore, a higher amount of silt and clay in the sediment at this station may also contribute to the effective deposition of PAHs (Table S-2). Relatively high levels of both parent and alkylated PAH homologues were also found at station TS5, which is approximately 20 miles from the Italian coast. This area is affected by the backward cyclonic gear that spreads contaminants introduced in the Adriatic by the Po valley watershed (Marini et al., 2015). Summed parent-PAH concentrations in the majority of coastal sediments, including Kaštela bay, were within the range that corresponds to the low medium contamination level, which is between slightly below 100 and slightly above 400  $\mu\text{g kg}^{-1}$ , d.w. (Tolosa et al., 1996; Lipiatou et al., 1997; Baumard et al., 1999; Gomez-Gutierrez et al., 2007; Barakat et al., 2011; Mzoughi and Chouba, 2011). Relatively high concentrations ( $>1000$  were  $\mu\text{g kg}^{-1}$ , d.w.) were found only at stations CS3 and CS10 in the coastal zone and at station KB3 in Kaštela Bay. At these stations, PAH levels were 2–6 times higher than at adjacent sites, indicating local hot spots identified near the town of Zadar (CS3), the site of a former chromium and carbide plant (CS10), and at the shipyard - industrial harbour of Split in Kaštela Bay (KB3). These concentrations are comparable to PAH levels reported for urbanised coastal areas (Benlahcen et al., 1997; Bertolotto et al., 2003; Di Leonardo et al., 2009). In Kaštela Bay, the local gradient is observed for all sampling periods, with concentrations decreasing with increasing distance from the eastern part, near an industrial port (station KB3), to the central part of the bay (station KB4). Furthermore, in the coastal area and Kaštela Bay, for most stations, PAH concentrations in sediments were within the range corresponding to the average pollution level generally found in areas under moderate anthropogenic pressures, for instance in the Black Sea (Wakeham et al., 1980), the eastern Mediterranean (Tsapakis et al., 2003; Tsapakis et al., 2006), Porto-Tores harbour in Sardinia (De Luca et al., 2004) and Daya Bay in China (Zhou and Maskaoui, 2003). Finally, very low coastal concentrations of parent-PAH ( $<150$   $\mu\text{g kg}^{-1}$ ) were determined only at two stations (CS1 and CS7) characterized by high sand content. Such levels correspond to those reported for more remote sea areas, with low pressures from urban and industrial activities, such as the Balearic Islands (127  $\mu\text{g kg}^{-1}$ , d.w.) and Corsica (87  $\mu\text{g kg}^{-1}$ , d.w.) (Baumard et al., 1998; Benlahcen et al., 1997).

High and extremely high concentrations were determined in the Šibenik Bay sediments. The lowest levels found were above 4000  $\mu\text{g kg}^{-1}$ , d.w. of parent-PAH, and these values compare to contamination levels in highly industrialised coastal areas in the Mediterranean and worldwide, such as Toulon Harbour (Benlahcen et al., 1997), Barcelona Harbour (Baumard et al., 1998), Napoli Harbour (Sprovieri et al., 2007) and the Bay of Mexico (Ponce-Vélez et al., 2006). The highest concentrations in the bay were found in the vicinity of the former ferroalloy factory (stations SB4 and SB8), indicating that this historical industrial activity was the main emission source of PAHs in Šibenik Bay. Very significant levels were also found in the harbour area and near-shore in the western part of the Šibenik urban centre (stations SB6 and SB3). The spatial distribution of PAH in the sediments suggests that contamination has spread over the entire bay. However, this contamination seems to remain in Šibenik Bay, given that the PAH concentrations at the closest station outside the bay (CS6), only 2.5 miles away from the entrance to the bay, are 10–20 times lower (alkyl and parent-PAHs respectively) than the lowest levels determined in the centre of the bay (station SB5). Indeed, limited circulation, water mass exchanges and the local hydrosedimentological regime indicate very poor sediment export to adjacent areas outside Šibenik Bay (Bužančić et al., 2016; Kušpilić, 2005).

Thus, it appears that the range of PAH concentrations in coastal and mid-Adriatic sediments spans over more than 2000 times between the lowest and the highest contamination levels. In this

area, the spatial distributions thus reflect the presence of the strong gradients at local and regional scale, in the contamination of sediments by PAHs. The major factor influencing sedimentary PAH distributions at local scale appears to be the distance from their known continental and coastal upstream emission sites (urban, industrial, harbour ...). At a regional scale, however, this distribution depends more on the routes of maritime entry of PAHs (riverine, atmospheric, naval ...) and their downstream dispersion, deposition dynamics and sediment type.

### 3.2. Characterization of PAH sources

The characterization of PAH sources in the environmental samples is generally based on the examination of their chemical composition, allowing the qualitative identification of source signatures (Stogiannidis and Laane, 2015) and also, ultimately, the quantitative apportionment of the amount of contaminants contributed by each source (Larsen and Baker, 2003; Lang et al., 2013). Such characterization might also be supported by the examination of the geographic distribution of PAH concentrations, which would eventually allow assignment of their emission point sources in the studied area. Both of these approaches are selectively used in this study.

#### 3.2.1. Geographic distributions

Based only on the geographic distribution of the sedimentary PAH concentrations in the coastal Adriatic, it was possible to reveal a few point emission sources of PAHs in the studied area. As already discussed above, in the coastal areas characterized by different levels of contamination (i.e. Šibenik Bay and the whole coastal survey including Kaštela Bay), PAH concentrations in the sediments are higher in the areas near emission sources, which may be present or past (Fig. S-1). Thus, in Šibenik Bay, very high levels were found at the stations clearly related to the local point source of PAHs emitted from the former ferroalloy industrial plant (stations SB4 and SB8) and also from mixed sources of PAH releases from urban and harbour/marina facilities (stations SB3, SB1 and SB6). Whereas, along the Croatian coast high concentrations were found near the Zadar urban centre (station CS3), a former metal (iron/chromium) plant (station CS9) and the industrial harbour of Split in Kaštela Bay (station KB3). All these sites should thus be considered as the “hot spots” of sediment contamination by PAHs along the Croatian coast.

#### 3.2.2. Source indicators and classification model-building

The relative PAH abundances, molecular indices and multivariate analysis allow identification and classification of PAH source profiles and contributions (Stogiannidis and Laane, 2015). The ratio of alkyl to parent compounds ( $\Sigma\text{Alkyl}/\Sigma\text{PAH}$ ) was used to assess pyrogenic or petrogenic sources of PAHs in sediments (Yunker et al., 2002). This ratio is sensitive to fresh petroleum releases and was used to distinguish pre- and post-spill contamination after major oil spill events (Short and Harris, 1996; Law et al., 1999; Tronczyński et al., 2004). The threshold values depend on which parent and alkylated homologues are used for calculation of the sum of their totals but, in general a lower than 0.5 ratios are related to pyrogenic sources, whereas a ratio above 1 is more often related to a petrogenic source. In the data presented here, the  $\Sigma\text{Alkyl}/\Sigma\text{PAH}$  ratio varies between 0.23 and 1.17 (Table S-5). The lowest values were found in Šibenik Bay indicating the strong contribution of pyrogenic PAHs, whereas the highest ratios were determined at four stations: Kaštela Bay in the industrial northern port of Split (KB3), at transect stations TS4 and TS6 (the first representing the route with highest shipping traffic density in the Adriatic and the second is the closest to the Italian coast, as discussed above, and is

influenced by the Po River loads) and at station CS2, i.e. one of the northernmost inner coastal sampling sites with relatively high PAH levels. The application of the  $\Sigma\text{Alkyl-PAH}/\Sigma\text{PAH}$  ratio also depends on the correlation of two variables (Tronczyński et al., 2004). The correlation of parent PAHs with their alkyl homologues thus allows to clearly distinguish the contamination by PAHs in Šibenik Bay from other areas (Fig. S-2).

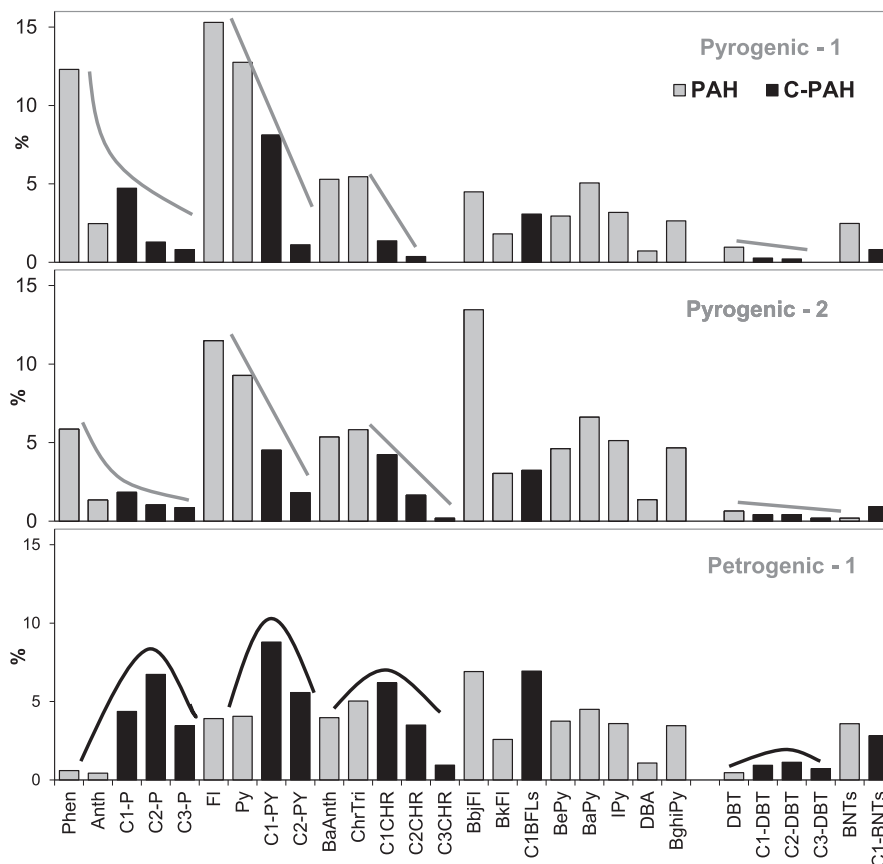
Discrete regression for the Šibenik site, definitely implies specific predominant sources in the bay and that PAH composition is different in the areas outside the bay, with a clearly higher relative contribution of alkyl homologues, indicating greater relative petrogenic inputs. This also suggests that parent against alkyl homologue correlations and ratios might be reliable PAH source indicators for both local and larger geographic areas, and that despite very high concentrations, PAHs from Šibenik indeed remain confined to the bay. Moreover, such indicators of PAH sources in sediments should be less sensitive to degradation/weathering processes, because of the use of summed concentrations of almost all PAHs and their determined homologues. In Šibenik Bay sediments, the indicators clearly withstand past contamination signatures from the ferroalloy plant. These correlations also show (Fig. S-2) that in Šibenik Bay the possible higher contribution of petrogenic PAH, with a relative higher proportion of alkyl homologues, may be inferred at the stations corresponding respectively to Šibenik marina (SB1), the entrance to the Šibenik port (SB 2 and SB7) and one of the samples from the Šibenik fisheries port (SB3) (Fig. S-2). Finally, added points of modelled source profiles of PAH from ALS statistics (see below) align well with the Šibenik regression line for two combustion profiles, as well as for all other stations with the regression line for a petrogenic source.

Analogous grouping among samples is obtained by principal component (PCA) and hierarchical cluster (HCA) analyses taking into account the relationships between the independent variables of all determined individual PAH compounds (Fig. S-3). The greatest distance was obtained between the Šibenik Bay stations and all other stations. However, higher variation and dissimilarities may be observed in Šibenik Bay, suggesting an overlap and combination of distinct PAH sources. Discrete clustering is found for the coastal survey among stations KB3, CS2, CS3 and CS9 that are characterized by higher contamination, in the vicinity of known emissions sources. These findings indicate overall that: geographical distribution, PAH source indices and explanatory multivariate statistics allow coherent categorization of sampling stations, according to the relative contributions of mainly petroleum versus combustion-derived PAHs in the sediments of the studied area. Distinctive characteristics of these sources and their quantitative proportion estimates in each area were further examined by the receptor environment model based on chemometric multivariate statistical analysis.

#### 3.2.3. Source profiles and contributions

Chemometric analysis involving receptor environment models allows the identification of source profiles (PAH fingerprints) and quantitative apportionment of such PAH sources. The algorithm used in the present estimations, is based on multivariate alternating least square (ALS) calculation using the iterative technique (Pirouette, Infometrix, 2014). PAH model source profiles, 2 combustion profiles and 1 petroleum profile, were obtained by alternative least square analysis (Fig. 2).

Both combustion profiles are characterized by higher abundances of unsubstituted PAHs and by “skewed” patterns of parent/alkyl-substituted compounds (phenanthrenes/anthracenes, fluoranthenes/pyrenes and chrysenes). In these profiles, greater alkylation homologues were less abundant ( $C1 > C2 > C3$ ). The reduced alkylation is consistent with the loss of alkyl side chains during the

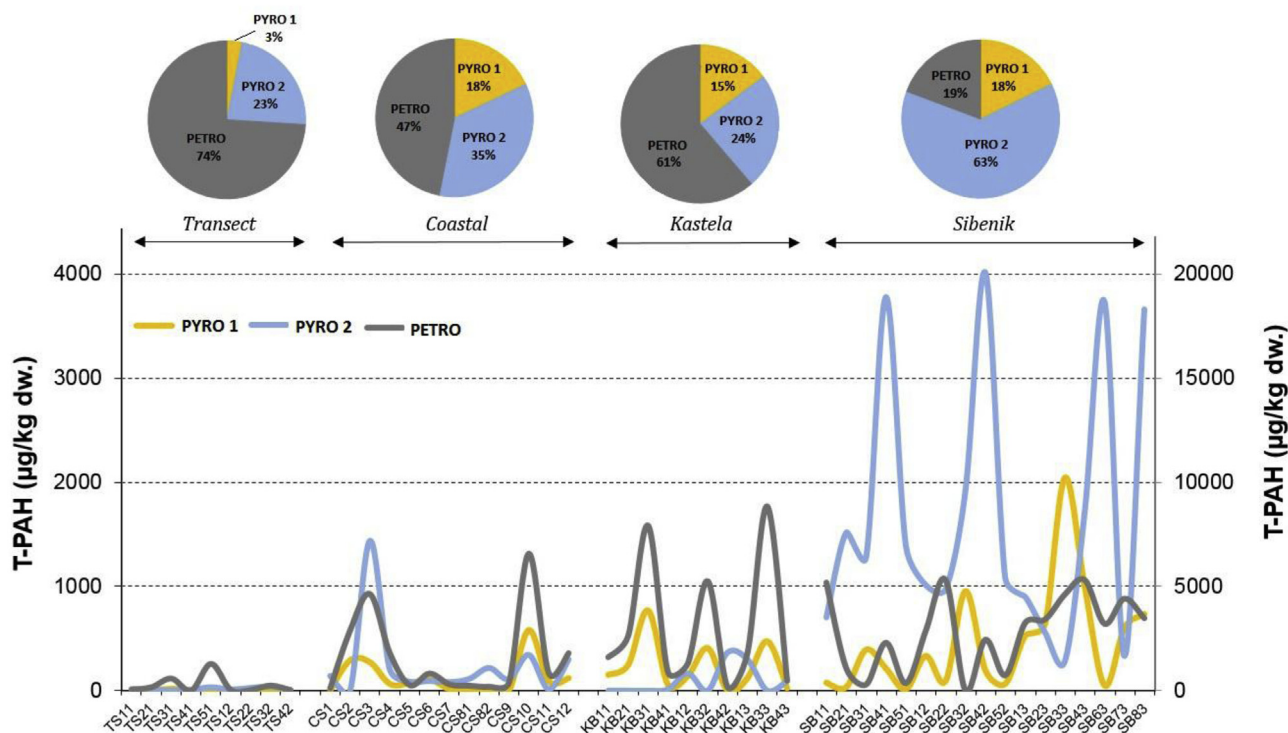


**Fig. 2.** PAH source profiles obtained by ALS Alternating Least Square calculation (Pirouette, Infometrix, 2014). Abundances (weight %) of parent individual compounds (PAH) and of summed alkyl-substituted homologues (C1 mono- C2 di- and C3 three-methyl substituted PAH). Unresolved by GC-MS PAH isomers are given together (triphenylene from chrysene and benzo[*b*]fluoranthene from benzo[*j*]fluoranthene). For PAH abbreviations see Table S-3.

combustion processes (Lima et al., 2005). Furthermore, different proportions of fluoranthene, pyrene, phenanthrene and benzo[*b+j*] fluoranthenes in two pyrogenic sources, probably discriminate also between different temperature combustion processes, such as motor vehicle engines and open burning (Tobiszewski and Namiesnik, 2012). In the range of higher molecular weight, the HMW-PAHs benzo[*e*]pyrene/benzo[*a*]pyrene (BePy/BaPy) ratio is lower than 1 for both pyrogenic profiles (Fig. 2), suggesting non-atmospheric routes of entry and/or that these compounds are not transported far from their emission source (Tobiszewski and Namiesnik, 2012).

In the petrogenic source profile, alkyl-substituted compounds were dominant, with characteristic “bell-shaped” patterns for phenanthrene/anthracene, fluoranthene/pyrene and chrysene suites of compounds. In this petrogenic profile, relatively abundant sulphur heterocycle homologues, such as alkyl-dibenzothiophenes, displaying a bell-shaped distribution may also be noted. However, the significant presence of non-substituted benzophthothiophenes (mainly benzo[*b*]naphtho[2,1-*d*]thiophene) may also indicate mixed sources of petrogenic and diesel-combustion emissions (Larsen and Baker, 2003). Furthermore, fairly elevated proportions of higher molecular PAHs (benzopyrenes, indeno[1,2,3-*cd*]pyrene (IPy) and benzo[*ghi*]perylene (BghiPy) may also imply a mixed source of PAH for this profile. For this reason, caution should be exercised when interpreting the quantitative results of PAH apportionment by multivariate receptor environment models (Larsen and Baker, 2003).

The quantitative apportionment of PAH source contributions reveals significant geographical differences (Fig. 3). Dominant petrogenic PAHs were found along the mid-Adriatic transect (approximately 74%) and in the Kaštela Bay (61%). In the coastal sediments, contamination is assigned about equally to petrogenic/pyrogenic sources of PAHs (47% and 53%, respectively), whereas in Sibenik Bay a very high percentage is apportioned to the combustion compounds (81%). Despite generally lower levels of petroleum hydrocarbons along the mid-Adriatic and the Croatian coast (Fig. 3), these results indicate that sediment contamination by petrogenic PAHs may be spatially more important. This may also be consistent with the pathways of petroleum-derived PAHs, which are more dispersed, originating from various oil spillages and all routine leaks that accompany diverse maritime activities (oil cargo, harbour operations, regular and seasonal transport ...). Whereas, the pyrogenic PAH inputs along the Croatian coast seem to be more confined, being associated mainly with the urban/industrial point sources (Fig. 3). The distribution of modelled concentrations of total PAHs, apportioned to three identified sources, shows the peaks of high levels of petrogenic and pyrogenic PAHs, found repeatedly at the same stations for all sampling periods in Kaštela Bay (station KB3 industrial port of Split) and in Sibenik Bay (SB4, former ferroalloy plant, Fig. 3). Thus, it appears that contamination by PAHs at these sites is not transient. The higher relative petrogenic contributions may also be seen in the sediments facing the marina in Sibenik Bay (station SB1) and more generally in the whole coastal area between Kaštela Bay and Dubrovnik (stations CS9, 10, 11 and



**Fig. 3.** Distributions of modelled total T-PAH concentrations ( $\mu\text{g}/\text{kg d.w.}$ ) apportioned into two pyrogenic and one petrogenic source in each studied area; the Šibenik Bay concentrations are given with right y-axis; Upper pies show summed weight percent of total source contributions for each area. All results are based on an alternative least square ALS-model.

12). These areas are definitely under high pressure by recreational coastal navigation. It also appears that the overall source contribution determinations obtained by the ALS model compare generally very well with the source indicators discussed above. The ratio of alkyl to parent PAH compounds ( $\Sigma\text{Alkyl}/\Sigma\text{PAH}$ ) correlates very well with the estimated percent contribution of the petrogenic PAH source, thus confirming that it is an excellent proxy for these source inputs (Fig. S-5).

However, pure source identification might be difficult and questionable. In receptor model approaches, generally, data sets do not contain end-member reference source profiles (Comero et al., 2009). PAH data reflect a mixture of sources and generally no single compound is the unique tracer of a particular source. Furthermore, as identified in this study, a characteristic profile of PAH sources assigns very broad classes (i.e. petroleum and combustion) that to a certain degree overlap in their profile identification. In addition, such PAH classes are themselves mixtures of compounds derived from multiple sources. Moreover, further identification, especially of combustion sources, is generally needed, in order to resolve PAHs derived from biomass burning and fossil fuel (coal and petroleum) combustion. This is valuable scientific information within the framework of the current efforts for global characterization of pyrogenic carbon in climate change impact studies. In sedimentary records, PAHs may be used as molecular markers, tracing fossil fuel-derived pyrogenic carbon (Hanke et al., 2017). This information is also required for management decisions concerning environmental measures. In the present calculations, no specific PAH source markers of wood combustion were used, such as selected alkylphenanthrene isomers. Likewise, certain heavy molecular weight (302 MW) compounds (known as gasoline and diesel combustion markers) were not included either (Ramdahl, 1983; Benner et al., 1995; Allen et al., 1998; Guillon et al., 2013). The addition of such compounds would possibly help to further

resolve characteristic source profiles and their contributions from our set of data. Additional PAH markers, which were analyzed in the Croatian sediments (such as retene, a series of dimethylphenanthrenes, naphtho-fluorathenes/pyrenes and dibenzopyrenes) will be used in further source characterization assessments. Nevertheless, the ALS method allowed us to assess the modelling power of individual compounds. The benzo[*b*+*j*]fluoranthenes and fluoranthene and pyrene compounds characterized two combustion sources, while the alkyl-substituted signature homologues (phenanthrenes/anthracenes, fluoranthenes/pyrenes and chrysenes and dibenzothiophenes) delineate an oil source profile. Consequently, these results provide preliminary reference data for source profiles and contributions concerning the contamination of marine sediment by PAHs in the mid-Adriatic and along the Croatian coast.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2018.06.095>.



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