

## Concentrations and origin of polycyclic aromatic hydrocarbons in sediments of the Middle Adriatic Sea

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*A total of 208 polycyclic aromatic compounds and their substituted homologues were investigated on eight stations along Croatia-Italy transect in the Middle Adriatic. PAC concentrations were higher in the coastal area than in the open sea area. The highest PAC concentrations were measured in the vicinity of the industrial harbor of Split while the lowest concentrations were observed on stations located in the open sea area. Polycyclic aromatic hydrocarbons were dominant group of compounds on each investigated station with contributions in total PAC concentration of more than 85%. S-PAH concentrations were higher than O-PAH concentration in each sample and tend to decrease as the distance from the coast increased. Contributions of O-PAH in total PAC concentrations were higher in the open sea sediments while S-PAH contributions were higher in the coastal sediment, indicating a different origin of O-PAH. Grain size analysis of the investigated sediments shows the dominance of fine fraction in sediments in the coastal area whereas sandy particles were a dominant fraction in the open sea sediments. TOC concentrations were higher in the open sea area where lower PAH concentrations were observed, indicating a different origin of PAC and TOC. PAH origin was evaluated by application of diagnostic ratios. Pyrogenic origin was determined only on one station whereas dominance of petrogenic PAHs was observed on the most of the stations in the open sea area. Marine traffic was suspected to be the main source of pollution in the open sea area.*

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**Key words:** *polycyclic aromatic compounds, PAH, sediments, diagnostic ratios, marine pollution, Adriatic Sea*

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are a large group of organic compounds that consist of two or more fused aromatic rings in their structure (VOLHARDT, 1999; EHRENHAUSER, 2015). Along with heterocyclic aromatic compounds, they form a large group of environmental pollutants of which many show potential toxicity to living organisms. PAHs are proved to have disruptive effects on the lymphatic system and hematopoietic activity (ATSDR, 1990b, SANTODONTO *et al.*, 1981). Chronic exposure to PAHs leads to mutagenesis, as they tend to incorporate in DNA structure causing mutagenesis and subsequent cancer formation.

Although some PAH compounds are formed naturally from biological precursors, most of the PAHs in the environment originate from anthropogenic activities such as transportation, power plants, industrial furnaces, coke and black carbon production, asphalt and petroleum cracking (NEFF, 1979). According to the origin, PAHs are commonly divided in natural PAHs, which are released into the environment from a natural source such as biogenesis; and PAHs of anthropogenic origin that are produced in various industrial and urban activities. Anthropogenic PAHs are further divided in petrogenic PAH compounds, produced during the low-temperature conversion of organic-rich material into the fossil fuel components, and pyrogenic PAHs, produced during the incomplete combustion of organic materials in the various high-temperature process. PAH mixtures emitted from petrogenic sources contain significant amount of alkyl-substituted PAH and PAHs of lower molecular weight, while mixtures emitted from pyrogenic sources are enriched with unsubstituted PAH compounds with more than 3 rings in their structure (GRIMMER *et al.*, 1981; GSCHWEND & HITES, 1981; GUO *et al.*, 2007; SICRE *et al.*, 1987; BUDZINSKI *et al.*, 1997; YUNKER *et al.*, 2002; TOBISZEWSKI & NAMIESNIK, 2012).

PAH can enter into marine environment directly, via accidental spillage of petroleum products, or indirectly, by riverine inputs, urban and industrial runoffs, atmospheric deposition

etc. Being highly hydrophobic, they tend to adsorb on suspended organic matter and sink through the water column until they finally settle in the bottom sediment (TSAPAKIS *et al.*, 2003; NEFF, 1979). Due to the high persistence toward degradation, PAHs tend to accumulate in sediments in high concentrations persisting toward degradation through long times.

PAHs have been subject of numerous research studies in the last three decades, since the U.S. Environmental Protection Agency (USEPA) included 16 PAH compounds on the list of priority pollutants in the environment, due to their high toxicity for living organisms (USEPA, 1980). High PAH concentrations were reported for the coastal sediments of highly industrialized and urbanized areas such as the big coastal cities and harbors (BENLACHEN *et al.*, 1997; BAUMARD *et al.*, 1998). Considerably lower concentrations were found in the open sea sediments and other remote areas where anthropogenic pressures are minimal or absent.

Many authors have studied PAH concentrations in the sediment of the Adriatic Sea. Values reported for the western Adriatic were in range 31-527 (GUZZELLA & DE PAOLIS, 1994), corresponding to the values determined in sediments in coastal areas of Chioggia and Ancona (MAGI *et al.*, 2012). Somewhat higher PAH concentrations were reported for the Gulf of Trieste (NOTAR *et al.*, 2001; HEATH *et al.*, 2006) whereas very high PAH concentrations were reported for the Venice lagoon (FATTORE *et al.*, 1997). While these research studies were mainly focused on the northern Adriatic basin and western Adriatic coast, only a few research studies of PAH concentration were conducted in the sediments of the eastern Adriatic Sea. The aim of the present study was to investigate distribution and sources of PAHs in sediment in the middle part of the eastern Adriatic Sea. Presented research provides preliminary results on PAH concentrations and will serve as a basis for further monitoring and research projects. Except for the PAHs, the list of the target compounds also included heterocyclic aromatic compounds of Sulphur and oxygen, which are commonly emitted with PAHs and can serve as an indicator of PAH origin. In order to find the most reliable indices

of PAH origin, different diagnostic ratios have been examined and the most probable source of pollution was suggested for the each location.

## MATERIAL AND METHODS

### Research area

PAH concentrations were studied on eight stations situated along the transect Croatia-Italy in the Adriatic Sea, as shown in Fig. 1.

The Adriatic Sea is a semi-enclosed basin connected with the Eastern Mediterranean through Otranto Strait (GRILLI *et al.*, 2013). It is commonly divided into northern, middle and southern Adriatic with the northern part being the shallowest. The middle Adriatic is deeper than the northern, reaching its maximum depth of 270 m in the Jabuka Pit. Southern Adriatic is the deepest part with the maximum depth of 1250 m. Mean surface circulation consists of cyclonic gyre flowing northward along the eastern side (Eastern Adriatic Current - EAC) and southward return flow along the Western side (Western Adriatic Current) (GRILLI *et al.*, 2013). The Northern Adriatic is highly affected by a large amount of fresh water that is introduced in the Adriatic by the Po River (MARINI *et al.*, 2015). In the northern Adriatic, Dense Water mass (Northern Adriatic Dense Water) is gener-

ated during the colder part of the year (autumn and winter), causing a cold bottom current over the Western Adriatic shelf. Transect Croatia (Split) – Italy (Mt. Gargano) is situated in the middle Adriatic, in the vicinity of the borderline between the middle and southern Adriatic. It encompasses the area of the Palagruža Sill and it is influenced by the movement of the Middle Adriatic Dense Water that is generated in Middle Adriatic and resides in the bottom layer of the Jabuka Pit. When a large amount of Middle Adriatic Dense Water is formed, it overflows the Jabuka Pit and joins Northern Adriatic Dense Water that flows toward the southeast (MARINI *et al.*, 2015). Formation and circulation of Northern Adriatic Dense Water and its overflowing of the Jabuka pit influences spreading and distribution of pollutants over the Palagruža Sill and along the Western Adriatic coast (MARINI *et al.*, 2015; GRILLI *et al.*, 2013; VILIBIĆ & ORLIĆ 2002; ARTEGIANI, 1997).

Research area encompasses three stations (S1, S2 and S3) in the coastal area and 5 stations (S4, S5, S6, S7 and S8) located in the open sea area. Station S1 is located in the north-eastern part of Kaštela Bay and is considered an area that is under the great anthropological pressure due to the various industrial and urban activities. The most intensive pressures on this location are from the cement factory, shipyard, industrial

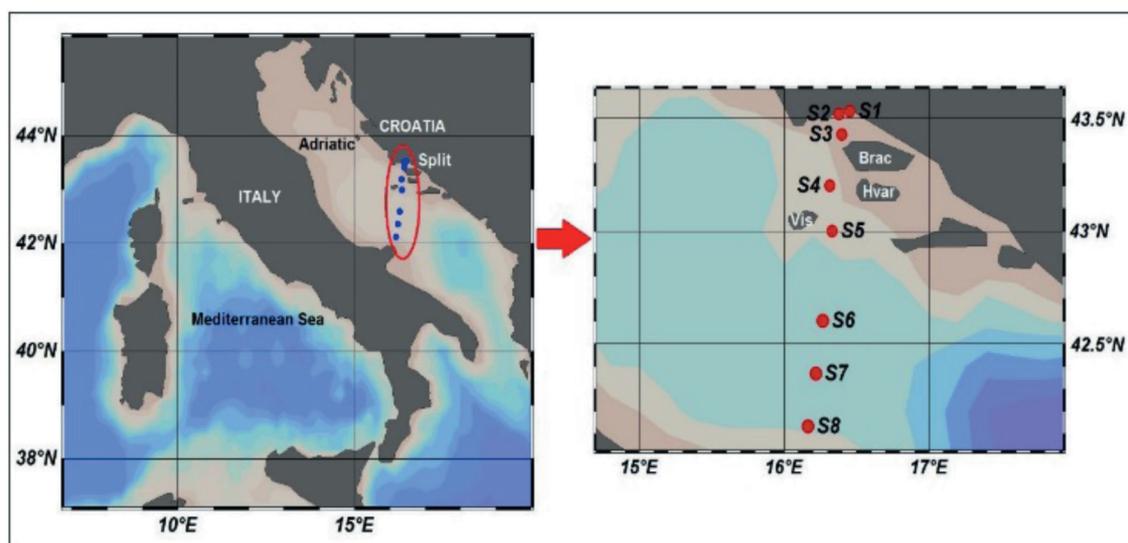


Fig. 1. Sediment sampling locations for determination of polycyclic aromatic compounds

Table 1. Sampling dates, geographic position and bottom depth at the investigated stations

STATION	SAMPLING DATE	BOTTOM DEPTH (m)	LATITUDE	LONGITUDE
<i>S1</i>	20.02.2013	18	43,5300N	16,4533E
<i>S2</i>	20.02.2013	38	43,5183N	16,3816E
<i>S3</i>	18.02.2013	52	43,4266N	16,3983E
<i>S4</i>	18.02.2013	78	43,2000N	16,3166E
<i>S5</i>	19.02.2013	105	43,0000N	16,3333E
<i>S6</i>	18.02.2013	175	42,6000N	16,2683E
<i>S7</i>	18.02.2013.	102	42,3666N	16,2200E
<i>S8</i>	18.02.2013	116	42,1333N	16,1666E

port and urban activities from the nearby cities. Station 2 is located in the middle of the bay and it is affected by anthropogenic activities. Inputs of freshwater by the Jadro River, in the north-eastern part of the bay, are responsible for the lower salinity in the bay if compared to the open sea sediments (ANĐELIĆ *et al.*, 2015). Station S3 is located in the coastal area of Split, between the islands Brač and Šolta. Stations S4, S5, S6 and S7 are the most distant from both eastern and western Adriatic coast, thus anthropogenic pressures are the least expressed. Marine transportation was recognized as the most important activity in this area. Station S8 is approximately 20 miles away from the western Adriatic coast and is also affected by marine transportation. Formation and circulation of Northern and Middle Adriatic Dense Waters contribute to pollution state in this area, bringing additional pollutants that are introduced in the Adriatic by the Po River (GRILLI *et al.*, 2013; MARINI *et al.*, 2015). Additional information for each location is given in Table 1.

Sediment samples were taken from the research vessel "BIOS DVA" during the campaign in February 2013. Approximately 100 grams of the top sediment layer was obtained from each station by the means of a grab sampler. Samples were wrapped in pre-cleaned aluminum foil and subsequently stored at the temperature of -20 °C. Frozen samples were transferred to a laboratory and lyophilised. Dry sediment samples were sieved through 0,2 mm screen and transferred to IFREMER laboratories where overall analyses were done. In order

to minimize contamination, during the whole procedure, plastic was strictly forbidden and all used laboratory equipment was thoroughly cleaned and heated on 450 °C before use.

### PAC analyses

Polycyclic aromatic compounds were determined according to the method developed by IFREMER laboratories (TRONCZYNSKI *et al.*, 2004). Ten grams of each sediment sample was weighed directly into the extraction cell and spiked with 150 µl of an internal standard solution containing two deuterated PAH compounds (Phenanthrene-d<sub>10</sub> and Benzo[*e*]pyrene-d<sub>12</sub>). Extraction was performed in ASE (Accelerated solvent extractor) with dichloromethane (DCM) as a solvent under 100°C and 138 Bar. Each sample was washed 5 times with DCM for two minutes. Sediment extracts were collected in two separate containers and joined upon the extraction. Samples were evaporated in a rotary evaporator and further concentrated under gentle nitrogen steam up to the volume of 1 ml. Concentrated extracts were spiked with small portions of isooctane and additionally evaporated until the final volume of 0,5 ml was reached.

Column chromatography with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as sorbents was employed for cleaning and fractionation. In order to control the cleaning process, 300 µL of standard solution was added in a separate column and afterward treated as the samples extracts. After addition of the samples, columns were washed with 36 ml of hexane for F1 fraction; 30 ml of hexane/DCM

mixture containing 10% of DCM for F2 and 20 ml of hexane/DCM containing 25% of DCM for F3 fraction. These three fractions were collected in the same flask, evaporated in the rotary evaporator and concentrated under nitrogen steam. Upon the concentration, residues were dissolved in isooctane up to the volume of 0,5 mL. Elementary sulphur was removed by addition of activated copper.

Sediment extracts were analyzed with an Agilent 6890 gas chromatograph (GC) using DB-5 MS capillary column (60 m long, 0,25 mm of internal diameter, phase thickness of 0,25  $\mu\text{m}$ ) in On column injection mode.

1  $\mu\text{L}$  of sample was injected with COMBI-PAL CTC autosampler. The oven was programmed as follows: holding on 50°C for 1 minute, from 50°C to 100°C at 15°C /min, from 100°C to 300°C at 4°C /min, holding at 300°C for 20 minutes. Helium with a flow rate of 0,8 ml/min was used as a carrier gas.

Identification of compounds was done with an Agilent 5973 N mass spectrometer operating in EI mode (70Ev, T=230°C) by the acquisition of the total mass spectra from 40-400 AMU and total ionic current (TIC) and additionally verified according to GC retention times. Quantitative analysis was done in selected ion monitoring (SIM) mode in relation to predeuterated compounds (Acenaphthalene-d<sub>10</sub>, Fluorene-d<sub>10</sub>, Pyrene-d<sub>10</sub>, Benzo[a]anthracene-d<sub>12</sub>

and Indeno[1,2,3-cd]pyrene-d<sub>12</sub>) added to the samples by an auto-sampler prior injection. Set of ten standard solutions with parent compounds concentration ranging from 0,005 to 8 ng  $\mu\text{L}^{-1}$  were used for calibration. A separate calibration curve was used for very low concentrations of PAHs in extracts (0,005 – 0,250 ng  $\mu\text{L}^{-1}$ ).

QA/QC procedure followed an internal protocol developed by IFREMER laboratories. Laboratory and field blanks were analyzed along with each batch of sediment samples. Overall, the analytical protocol was controlled by use of a surrogate standard solution containing phenanthrene-d<sub>10</sub> and benzo[e]pyrene-d<sub>12</sub> added to each sample before extraction, which enable to verify losses of analytes of interests during the entire procedure. Samples with recoveries below 70% were rejected and reanalyzed.

Standard reference materials (SRM 1491 and SRM 2977) from the National Institute of Standards and Technology-NIST were incorporated within a batch of sediment samples. The method detection limits were individually calculated for each sample. Laboratory proficiency for PAH analysis is also evaluated through regular participation in the QUASIMEME (Quality assurance of Information for Marine Environmental Monitoring in Europe) exercises. List of target polycyclic aromatic compounds, abbreviations and internal standards used for quantification are shown in Table 2.

Table 2. List of parent and alkyl-substituted PAHs, sulphur heterocyclic aromatic compounds and oxygen heterocyclic aromatic compounds determined in sediment samples; abbreviation, molecular weight and internal standard used as a reference

COMPOUND NAME	ABBREVIATION	MW	INTERNAL STANDARD
<b>PAHs and alkylated homologues</b>			
Naphtalene	Na	128	Acenaphthene-d <sub>10</sub>
C1-Naphtalenes	C1-N	142	Acenaphthene-d <sub>10</sub>
C2-Naphtalenes	C2-N	156	Acenaphthene-d <sub>10</sub>
C3-Naphtalenes	C3-N	170	Acenaphthene-d <sub>10</sub>
C4-Naphtalenes	C4-N	184	Acenaphthene-d <sub>10</sub>
Acenaphthene	ACE	152	Acenaphthene-d <sub>10</sub>
Acenaphthylene	ACY	154	Acenaphthene-d <sub>10</sub>
Fluorene	F	166	Fluorene-d <sub>10</sub>
C1-Fluorenes	C1-F	180	Fluorene-d <sub>10</sub>

(Cont'd Table 2)

C2-Fluorenes	C2-F	194	Fluorene-d <sub>10</sub>
Anhtracene	ANT	178	Fluorene-d <sub>10</sub>
Phenanthrene	PHE	178	Fluorene-d <sub>10</sub>
C1- Phenanthrene	C1-PHE	192	Fluorene-d <sub>10</sub>
C2- Phenanthrene	C2-PHE	206	Fluorene-d <sub>10</sub>
C3- Phenanthrene	C3-PHE	220	Fluorene-d <sub>10</sub>
Fluoranthene	FLA	202	Pyrene-d <sub>10</sub>
Pyrene	PY	202	Pyrene-d <sub>10</sub>
C1-Pyrenes	C1-PY	216	Pyrene-d <sub>10</sub>
C2-Pyrenes	C2-PY	230	Pyrene-d <sub>10</sub>
Retene	RET	219	Pyrene-d <sub>10</sub>
Perylene	PER	252	Benzo[a]anthracene-d <sub>12</sub>
Benzo[a]anthracene	BaA	228	Benzo[a]anthracene-d <sub>12</sub>
Chrysene	CHR	228	Benzo[a]anthracene-d <sub>12</sub>
C1-Chrysene	C1-CHR	242	Benzo[a]anthracene-d <sub>12</sub>
C2-Chrysene	C2-CHR	256	Benzo[a]anthracene-d <sub>12</sub>
C3-Chrysene	C3-CHR	270	Benzo[a]anthracene-d <sub>12</sub>
Benzo[a]pyrene	BaP	252	Benzo[a]anthracene-d <sub>12</sub>
Benzo[e]pyrene	BeP	252	Benzo[a]anthracene-d <sub>12</sub>
Dibenzo[a,e]pyrene	DBP	302	Benzo[a]anthracene-d <sub>12</sub>
Benzo[b+j+k]fluoranthene	BFL	252	Benzo[a]anthracene-d <sub>12</sub>
C1-Benzofluoranthenes	C1-BFL	266	Benzo[a]anthracene-d <sub>12</sub>
Naphto[1,2-k]fluoranthene	NaphtoFL	302	Indeno[1,2,3-cd]pyren-d <sub>10</sub>
Benzo[ghi]perylene	BPER	276	Indeno[1,2,3-cd]pyren-d <sub>10</sub>
Dibenzo[a,h]anthracene	DBA	278	Indeno[1,2,3-cd]pyren-d <sub>10</sub>
Indeno[1,2,3-cd]pyrene	IP	276	Indeno[1,2,3-cd]pyren-d <sub>10</sub>
Coronene	COR	300	Indeno[1,2,3-cd]pyren-d <sub>10</sub>
C-302	C-302	302	Indeno[1,2,3-cd]pyren-d <sub>10</sub>
<b>S-PAH and alkylated homologues</b>			
Dibenzothiophenes	DBT	184	Fluorene-d <sub>10</sub>
C1-Dibenzothiophenes	C1-DBT	198	Fluorene-d <sub>10</sub>
C2-Dibenzothiophenes,	C2-DBT	212	Fluorene-d <sub>10</sub>
Benzo[b]naphtothiophenes	BNTs	234	Pyrene-d <sub>10</sub>
C1- Benzo[b]naphtothiophenes	C1-BNTs	248	Pyrene-d <sub>10</sub>
<b>O-PAH and alkylated homologues</b>			
Dibenzo[b,d]furan	DBF	168	Fluorene-d <sub>10</sub>
C1 - Dibenzo[b,d]furan	C1-DBF	182	Fluorene-d <sub>10</sub>
C2 - Dibenzo[b,d]furan	C2-DBF	196	Fluorene-d <sub>10</sub>

### Grain-size distribution and total organic carbon (TOC) of the sediment

Grain-size distribution of the sediment was determined by the combined method of sieving and aerometric measurements as described by Casagrande (CASAGRANDE, 1948). Sediment was classified according to the Wentworth scale and presented as the amount of gravel (>0,2 mm), sand (0,125-0,2 mm) and mud (<0,125mm) (WENTWORTH, 1922; FOLK, 1954). Mud was calculated as a sum of silt (0,063-0,125 mm) and clay (<0,063). TOC in the sediment was determined by the combined method of chemical and thermal oxidation. Samples were treated with hydrochloric acid for one hour in order to remove carbonate fraction. Afterward, sediment samples were thermally oxidized in the furnace at 375 °C with an airflow rate of 200 ml/min. TOC was finally determined upon the concentration of combustion-derived CO<sub>2</sub>.

### Assessment of PAHs origin

PAHs origin was evaluated by calculation of concentration ratios between various PAH compounds. These ratios are often referred to as diagnostic ratios or diagnostic indices as their value is used to differentiate between various PAH sources. In order to accurately ascribe certain ratio value with a possible source of pollution, it is necessary to know the structure of PAH mixtures emitted from different sources. For this purposes, PAH mixtures generated during the combustion of different organic materials under different conditions were extensively studied which isolated PAH molecules that can be used as an indicator of origin. Concentration ratios of isomers with same molecular weight have been widely used in order to differentiate between petrogenic and pyrogenic PAH pollution (GRIMMER *et al.*, 1981; GSCHWEND & HITES, 1981; GUO *et al.*, 2007; SICRE *et al.*, 1987; BUDZINSKI *et al.*, 1997;

YUNKER *et al.*, 2002). These ratios are temperature dependent since PAH isomers formed during the low temperature process (< 200 °C) are more stable than the isomers formed during the high-temperature combustion. Therefore, prevalence of less stable isomer in PAH mixture indicates high-temperature process as the most probable source. Following isomer pairs of the same molecular weight were used: PHE/ANT, FLA/PY, BaA/CHR and IP/BghiPer.

Other indicators for addressing PAH pollution sources are concentration ratios between parent PAHs and their alkylated counterparts (LEHNDORF & SCHWARK, 2009; GSCHWEND & HITES 1981; KIM *et al.*, 2008; LUO *et al.*, 2008; ELMQUIST *et al.*, 2007). Unburned petroleum and other fossil fuels contain a significant amount of alkylated PAH, thus, their dominance over unsubstituted homologues is a potential indicator of petrogenic origin of pollution. In this study, the relation between phenanthrene, pyrene, chrysenes and their alkylated homologues were studied in order to distinguish between different PAH source. Concentration ratio between total parent PAHs and total alkylated homologues had also been applied.

Finally, PAH origin was evaluated by application of pyrogenic index (PI) and fossil fuel pollution index (FFPI). Pyrogenic index (PI) is the ratio of the sum of the concentrations of unsubstituted 3-6 rings PAH, enlisted on EPA 16 priority list, to the sum of the concentration of the five alkylated homologues: naphthalenes, fluorenes, dibenzotiofenenes, phenanthrenes and chrysenes (WANG *et al.*, 1999b). PI values are higher for pyrogenic sources whereas for low PI values petrogenic sources are more likely.

Fossil fuel pollution index (FFPI) evaluates the contribution of fossil fuels to the PAH sediment concentrations using the ratio between the sum of characteristic petrogenic PAHs and total PAH concentration. Following mathematical expression was used for FFPI calculations:

$$FFPI = \frac{N+C1N+C2N+C3N+C4N+DBT+C1DBT+C2DBT + \frac{PHE+C1PHE}{2} + C2PHE + C3PHE}{TPAH}$$

Index values close to zero correspond with the most pyrogenic PAH mixtures while for the unburned fossil fuel this value is close to one

(IQBAL *et al.*, 2008; STOUT *et al.*, 2001b). Petrogenic sources contribution to overall PAH concentration increases as the index value increases.

## RESULTS AND DISCUSSION

### PAC concentrations and composition of PAC mixtures in sediments

Concentrations of polycyclic aromatic hydrocarbons (PAH), sulfur containing heterocyclic aromatic compounds (S-PAH) and oxygen-containing heterocyclic compounds (O-PAH) determined on investigated stations are shown in Table 3. PAH concentrations ranged from  $35,46 \mu\text{g kg}^{-1}$  (S4) to  $2274,24 \mu\text{g kg}^{-1}$  (S1) whereas total concentration of polycyclic aromatic compounds (PAC) ranged from  $39,93 \mu\text{g kg}^{-1}$  (S4) –  $2663,27 \mu\text{g kg}^{-1}$  (S1). Composition of PAC mixture with contributions of PAH, O-PAH and S-PAHs in the sediment of each station area shown in Fig. 2.

Highest PAC concentrations were measured on S1 station, situated in Kaštela Bay, where PAH accounted for 85,39% of total PAC concentrations in sediment (Fig. 2). High concentrations of PAC were also observed on S8 station, located approximately 20 miles from the Monte Gargano (Italian coast). PAH concentrations on this stations were  $991,88 \mu\text{g kg}^{-1}$  contributing to total PAC concentrations with 93,43%. PAHs were a dominant group on each station, contributing to total PAC concentration with more than 85%. The highest PAH contribution were determined on S3 station where PAHs accounted for 94,89% of total PAC concentrations (Fig. 2).

Concentrations of total S-PAH in the investigated sediments ranged from  $0,99 \mu\text{g kg}^{-1}$  (S6) to  $344,68 \mu\text{g kg}^{-1}$  (S1). Higher concentrations were determined in sediments that are more close to the coastal zone where higher concentrations of total PAC were also measured (Table 3). In the

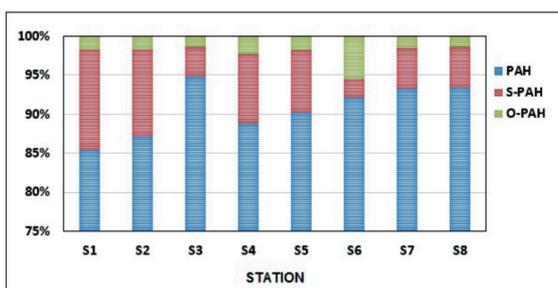


Fig. 2. Relative contributions of PAH, S-PAH and O-PAH to total PAC concentration in the investigated samples

most of the samples, C1-BNTs were dominant S-PAH compound, except for the two stations in Kaštela Bay where the dominance of C2-DBT with concentrations of  $92,13 \mu\text{g kg}^{-1}$  (S1) and  $16,64 \mu\text{g kg}^{-1}$  (S2) was observed. Methylated DBT were dominant compounds on S4 station where C2-DBT concentrations were equal to C3-DBT concentration ( $0,91 \mu\text{g kg}^{-1}$ ).

If S-PAH contributions to total PAC concentration in sediments were observed (Fig. 2), it is evident that highest contributions of this fraction were found in coastal sediments where the highest absolute concentrations of S-PAH were also determined. On S1 station S-PAH attributed for 12,98% of total PAC concentration whereas on S2 station, this contribution was somewhat lower, 11,16% respectively. On S6 station, S-PAH contribution was the lowest (2,31%) while on the rest of the stations, S-PAH contribution were within range 3,81 – 8,88%. In general, concentrations and relative amounts of sulfur-containing PAC tended to decrease as the distance from the coast increased.

Concentrations of non-substituted DBF were higher than the concentrations of its methylated counterparts on the majority of the stations (Table 3). Concentration range for parent DBF was within  $0,55$  (S4) –  $19,86 \mu\text{g kg}^{-1}$  (S1) while sum of the methyl and dimethyl DBF ranged from  $0,27$  (S5) -  $24,49 \mu\text{g kg}^{-1}$  (S1). C1-DBF were found to be dominant O-PAH compounds only on S6 station. Similar to PAH and S-PAH, concentrations of O-PAH were higher on the stations that are closer to the coastal zone. On S1 station,  $44,35 \mu\text{g kg}^{-1}$  of total O-PAH were measured, whereas on the S2 station O-PAH concentrations were  $9,79 \mu\text{g kg}^{-1}$ . Somewhat higher O-PAH concentrations were also found in the sediment of the S8 station ( $13,84 \mu\text{g kg}^{-1}$ ) while in the open sea stations (S4 and S5), O-PAH concentrations were below  $1 \mu\text{g kg}^{-1}$ .

Although the highest absolute concentrations of O-PAH were measured on S1 station, contributions of this fraction increased as the distance from the coast increased (Fig. 2). The highest contribution was observed on S6 stations where O-PAH accounted for 5,54% of total PAC concentrations. Open sea sediments

Table 3. Concentrations of polycyclic aromatic hydrocarbons, heterocyclic aromatic compounds of sulphur and oxygen ( $\mu\text{g kg}^{-1}$ ) with detection limits and recovery factors for two deuterated internal standards

STATION	S1	S2	S3	S4	S5	S6	S7	S8
Units	$\mu\text{g kg}^{-1}$							
LOD	4,12E-04	1,67E-04	9,50E-05	3,10E-05	3,40E-05	3,90E-05	3,40E-05	3,90E-05
<b>PAH</b>								
Na	13,98	3,56	1,09	0,22	0,35	0,22	2,13	12,56
C1-N	52,04	6,23	1,05	0,75	0,81	0,91	5,19	26,51
C2-N	113,75	14,69	2,36	1,13	2,05	5,92	7,08	42,38
C3-N	103,11	13,08	1,74	1,00	1,48	6,72	5,06	24,94
C4-N	51,33	8,19	0,47	0,64	0,47	3,43	3,06	17,60
ACY	2,31	0,54	0,19	0,00	0,06	0,00	0,15	0,86
ACE	9,68	1,14	0,25	0,08	0,05	0,00	0,20	0,85
F	17,50	3,22	0,78	0,18	0,23	0,20	0,43	4,27
C1-F	55,55	5,78	0,99	0,89	0,38	2,22	2,11	14,07
C2-F	65,35	7,39	0,49	2,50	0,54	4,49	2,19	11,42
PHE	90,44	20,75	8,05	1,21	1,98	1,13	7,21	19,81
ANT	26,90	6,16	2,17	0,24	0,17	0,20	0,27	1,95
C1-PHE	126,51	28,57	6,55	1,19	2,95	1,19	11,04	37,93
C2-PHE	157,62	31,70	4,53	0,75	1,14	1,01	8,26	36,29
C3-PHE	105,34	22,41	1,83	1,63	1,16	0,36	4,46	25,25
FLA	122,58	34,23	12,48	1,90	1,15	0,73	3,27	17,33
PY	120,44	32,57	10,46	1,45	1,27	0,77	3,13	21,00
RET	35,48	9,32	2,18	0,43	0,45	0,16	1,66	22,37
C1-PY	164,82	37,42	9,33	1,14	1,48	0,37	8,21	41,43
C2-PY	121,78	17,51	2,95	1,50	1,25	0,00	4,36	21,85
BaA	47,39	11,97	8,47	0,78	0,86	0,20	3,01	11,99
CHR	65,08	11,28	9,09	1,07	1,16	0,38	4,23	11,89
C1-CHR	89,54	20,53	5,15	1,03	1,19	0,25	5,15	28,90
C2-CHR	92,55	12,99	2,76	1,00	1,07	0,00	5,01	35,82
C3-CHR	21,34	3,25	0,00	0,01	0,51	0,00	1,06	15,63
BFL	132,48	49,43	26,21	2,96	5,13	2,06	13,10	89,19
C1-BFL	84,23	19,54	7,01	1,24	4,05	0,16	10,01	80,79
BeP	44,85	16,91	8,67	1,12	1,42	0,28	5,40	36,34
BaP	41,57	13,41	10,76	1,04	1,07	0,25	2,04	15,74
PER	23,03	7,58	3,97	0,56	1,04	0,28	3,10	83,47
IP	25,85	12,55	8,21	1,86	3,06	1,07	7,18	40,45
DBA	8,66	3,06	2,14	0,29	0,55	0,17	1,07	9,01
BPER	13,83	9,47	7,28	1,13	1,85	0,51	4,03	25,85
DBP	2,26	1,37	1,03	0,24	0,38	0,12	1,00	5,80
COR	2,25	1,56	1,54	0,53	1,22	0,00	4,30	21,87
C1-302	22,83	10,63	9,16	1,78	3,88	4,01	15,77	78,46
<b>S-PAH</b>								
DBT	28,09	6,30	1,49	0,22	0,23	0,15	0,71	3,38
C1-DBT	63,10	9,95	0,68	0,44	0,54	0,00	1,01	5,97
C2-DBT	92,13	16,64	0,80	0,91	1,09	0,08	1,63	10,87
C3-DBT	56,31	12,22	0,29	0,91	0,57	0,09	1,13	6,84
BNTs	31,76	8,95	1,76	0,56	0,69	0,26	2,22	9,94
C1-BNTs	73,29	11,13	2,25	0,50	1,10	0,41	2,38	18,45
<b>O-PAH</b>								
DBF	19,86	4,56	1,57	0,55	0,68	0,90	1,54	8,99
C1-DBF	13,91	3,49	0,72	0,30	0,22	1,49	0,82	3,98
C2-DBF	10,58	1,73	0,20	0,07	0,05	0,00	0,32	0,87
T-PAC	<b>2663,27</b>	<b>584,97</b>	<b>191,15</b>	<b>39,93</b>	<b>53,02</b>	<b>43,15</b>	<b>176,67</b>	<b>1061,17</b>
T-PAH	<b>2274,24</b>	<b>510,00</b>	<b>181,39</b>	<b>35,46</b>	<b>47,87</b>	<b>39,77</b>	<b>164,91</b>	<b>991,88</b>
RF Phenanthrene $d_{10}$ (%)	87,3	89,1	72,60	70,30	75,80	81,70	78,70	70,17
RF Benzo[e]pyrene $d_{12}$ (%)	71,2	73,1	70,30	73,50	95,00	91,60	81,40	75,16
RF average (%)	<b>79,25</b>	<b>81,1</b>	<b>71,45</b>	<b>71,9</b>	<b>85,4</b>	<b>86,65</b>	<b>80,05</b>	<b>72,67</b>

displayed higher contributions of O-PAH than stations near the coastal area, which was probably due to the different properties and different environmental behavior of O-PAH if compared with PAH. O-PAH are the most soluble group of polycyclic aromatic compounds; hence, their transport through sediment is enhanced if compared to other investigated groups. Furthermore, O-PAH are intermediate products of PAHs biodegradation, thus enhanced biodegradation rates in the open sea sediment could be another reason for higher O-PAH contributions. If bottom morphology of the investigated area was taken into account, former explanation is more likely as it was shown that sea depth gradually increases towards the open sea but in the vicinity of the S3 station depth suddenly decreases forming a barrier for sediment exchange between coastal and open sea area (BOGNER & MATIJEVIĆ, 2016).

Results show that absolute concentrations of heterocyclic compounds decreased when approaching open sea regions, which is due to the lower anthropogenic pressures on these stations if compared to the coastal ones. If, however, contributions of these groups to the total PAC concentration were observed, enrichment of the sediment with O-PAH in open sea regions is noticed whereas S-PAH contributions decreased as the distance from the coast increased. The probable explanation is that S-PAHs are released from the same sources as PAH, thus, areas with higher PAH concentration would also contain higher S-PAH concentrations.

Contrary to the S-PAH, O-PAHs show different environmental behavior than PAH compounds. The oxygen atom in O-PAH structure is responsible for the enhanced polarity of these compounds allowing more efficient transport through the water bodies. Furthermore, these substances are also formed by PAH degradation, thus, their concentration cannot be predicted upon PAH since O-PAHs are formed while PAHs are being degraded causing O-PAH concentrations to increase as PAH concentration decrease. (LUNDSTEADT *et al.*, 2007).

The highest PAH concentrations were observed on S1 station, situated in the northeastern part of Kaštela Bay (Table 3). This station is

nearest to the coast and is under intense anthropogenic pressures, mostly derived from transportation, industry and urban activities of the city of Split. Concentrations of PAH decreased as the distance from the Eastern coast increased, reaching minimal value on S4 station (35,38  $\mu\text{g kg}^{-1}$ ). Afterward, total PAH levels gradually increased by approaching the western Adriatic coast. Low PAH concentrations were measured on S4, S5, and S6 stations, located in the open sea area and most distant from both, Eastern and Western coast (Table 3).

Obtained results are in good accordance with earlier research of PAHs in the Adriatic. Similar PAH values were reported for the sediments along the western Adriatic coast (GUZELLA & DE PAOLIS, 1994), for the Gulf of Trieste (NOTAR *et al.*, 2001; HEATH *et al.*, 2006) and for the coastal area of Chioggia and Ancona (MAGI *et al.*, 2002.). Considerably higher PAH concentrations were reported for the areas under greater anthropogenic pressure such as Venice lagoon, with PAH concentration ranging from 184 to 201678  $\mu\text{g kg}^{-1}$  (FATTORE *et al.*, 1997) and Bay of Rijeka where PAH concentrations were from 52 to 12532  $\mu\text{g kg}^{-1}$ . (ALEBIĆ-JURETIĆ, 2011) Although a lot of research of PAHs in northern and western Adriatic was performed, there is a lack of recent data on PAHs in sediments of the eastern Adriatic. This is especially true for the middle and south part of the eastern Adriatic where only one research on PAHs was conducted in the last three decades. Back then, maximum PAH concentration was 2000  $\mu\text{g kg}^{-1}$  (DUJMOV *et al.*, 1994) which was the total PAH concentration in the sediment of Kaštela Bay, measured by fluorimeter and expressed as Chrysene equivalents. Even though this method is less accurate and less sensitive when compared to mass spectrometry, obtained results were in good accordance with results provided by the current study. If compared with other parts of Mediterranean Sea, these results show that the most of the sediment PAH concentrations correspond with those reported for the Black Sea (WAKEHAM *et al.*, 1996) and Eastern Mediterranean (TSAPAKIS *et al.*, 2003). Obtained data are also in good accordance with PAH values reported for the world sea sedi-



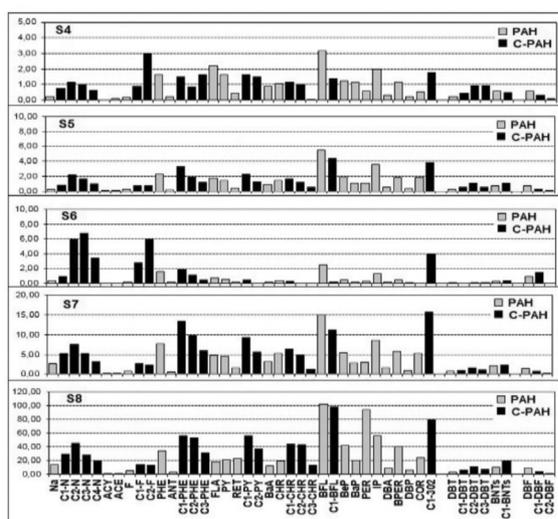


Fig. 4. Fingerprint pattern of polycyclic aromatic hydrocarbons determined for the stations in open sea area

C3-N accounted for 16,91% of total PAH concentration. The concentration of C2-N was 5,92  $\mu\text{g kg}^{-1}$  which was equal to the concentration of C2-F, contributing to total PAH concentration with 14,88% each. Naphthalene and its alkylated homologues, as the smallest PAH molecules, are the least stable among all PAH compounds. The half-life of naphthalene in marine sediments is 0,3 days - 129 days whereas for the more complex PAH compounds this time is much longer; e.g. half-life of benzo[*a*]pyrene is 3-58 years depending on environmental conditions such as temperature, oxygen amount and microbial populations (PAGE *et al.*, 1993). Due to the low persistence toward degradation, high naphthalene concentrations could indicate pollution of more recent dates, although caution is advised when interpreting naphthalenes concentration, as these compounds are the most common laboratory contaminant. Dominant PAH compounds in sediment of S7 station were C1-302 (15,77  $\mu\text{g kg}^{-1}$ ), followed by BFL (13,10  $\mu\text{g kg}^{-1}$ ), C1-PHE (1,19  $\mu\text{g kg}^{-1}$ ) and C1-BFL (10,01  $\mu\text{g kg}^{-1}$ ).

BFL, with a concentration of 89,19  $\mu\text{g kg}^{-1}$ , were dominant PAH on S8 station, followed by C1-BFL with a concentration of 80,77  $\mu\text{g kg}^{-1}$ . High concentrations were also observed for a C1-302 fraction (78,46  $\mu\text{g kg}^{-1}$ ). Perylene concentration on S8 station was 83,47  $\mu\text{g kg}^{-1}$  contributing to total PAH concentration with

8,42% which can be a potential indicator of biogenesis on this location as perylene is naturally produced by bacterial activity (PAGE *et al.*, 1996; TOLOSA *et al.*, 2004; LIMA *et al.*, 2005).

When summarized, obtained results show that BFL were dominant PAH compounds on the majority of the investigated station. These compounds are emitted in high extent from automobile exhaust and coke combustion process and are typically used as an indicator of pyrogenic origin (LEHNDORF & SCHWARK, 2009; KIM *et al.*, 2008; LUO *et al.*, 2008; ELMQUIST *et al.*, 2007). However, BFL can also originate from natural sources such as vascular land plants production or termite activity (TOBISZEWSKI & NAMIESNIK, 2012). It is assumed, however, that BFL are of anthropogenic origin as their dominance in the open sea sediments can be hardly linked to terrestrial activities. Contributions of C1-302 were also high in all sediment samples. Absolute concentrations of this fraction decreased as the distance from the coast increased, while on the contrary, relative amounts of C1-302 fraction increased as the distance from the eastern coast increased. The highest contribution was observed on S6 station where C1-302 accounted for 10,09% of total PAH. C1-302 contributions were also high on S5 (8,11%) and S7 (9,57%). The lowest contribution was observed on S1 station, where this fraction accounted for only 1,01% of total PAH concentrations. C1-302 fraction contains methylated isomers of PAH with six rings in their structure. This is the heaviest crude oil fraction typically contained in fuel oil and bituminous resins (STOUT & WANG, 2007). Because the higher contributions of this fraction were observed in open sea sediments, it could be assumed that C1-302 originate from ship fuel since marine transport is the most intense anthropogenic activity in the open sea regions. Increased relative amount of this fraction in the open sea sediments could be also explained by its high persistence. Degradation rates of PAH decrease with increased molecular weight of the compound, causing enrichment of sediment with heavier PAH fraction (NEFF, 1978; NRCC, 1983). In vitro tests of PAH behavior in sediments under different environmental conditions

demonstrated that high salinity values (above 37‰ or equal) negatively affect degradation rates of PAH compounds (MARINI & FRAPACINI, 2013). Molecules with higher molecular weight were more influenced by salinity fluctuations, although persistence of all PAH compounds toward degradation was enhanced at higher salinity values. Enhanced persistence of PAH toward degradation in the areas with higher salinity could be the reason for sediment enrichment with heavier PAH compounds in the open sea regions since the coastal zone is more influenced by the riverine inputs resulting in lower salinity in this area (MEANS, 1995; MARINI & FRAPACINI, 2013).

Perylene is considered as PAH of natural origin that is formed from biogenic precursors, although a considerable amount of perylene is also produced during the combustion (LIMA *et al.*, 2005). If perylene contribution to the total concentration of 5-rings PAH is greater than 10%, it can be considered of natural origin. PAH mixtures emitted during the combustion typically contain a small amount of perylene when compared to other PAH with 5 rings in their structure (PAGE *et al.*, 1996; TOLOSA *et al.*, 2004). Perylene contribution in total 5-ring PAH concentration was smaller than 10% at each station except for S8 station, where perylene accounted for more than 40% of total 5-rings PAH concentration, indicating the natural origin of this compound. This result also suggests strong biogenic/diagenetic activity on this station as these two processes are considered the main natural perylene sources.

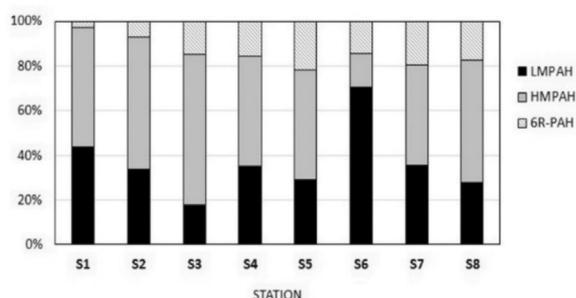


Fig. 5. Relative amounts of PAHs with low molecular weight (LMPAH), PAHs with high molecular weight (HMPAH) and PAHs with 6 rings (6R-PAH) in the structure

The relative amount of low molecular weight PAHs - LMPAH (2 and 3 ring PAH), high molecular weight PAH - HMPAH (4 and 5 ring PAH) and 6-ring PAH in the investigated samples are shown in Fig. 5. High LMPAH contributions to total PAH concentration in sediments were determined on S6 station, where this fraction accounted for 70,41% of total PAH concentration; and S1 station, where LMPAH accounted for 43,59%. The lowest contribution of this fraction was observed on S3 station where LMPAH accounted for 17,94% of total PAH concentrations. On the rest of the investigated stations, LMPAH contributions to total PAH concentration in sediments were higher than 20%. This light PAH fraction is a typical component of unburned fossil fuels and other petroleum-derived products and usually indicates PAH mixtures of petrogenic origin (PAGE *et al.*, 1996; STOUT & WANG, 2007). If compared to HMPAH, this fraction is more susceptible to both, biodegradation and photodegradation, which is the reason for the enrichment of the sediments with heavier PAH fraction during the time (NEFF, 1979; SICRE *et al.*, 1987). If this was taken into account, it can be assumed that PAH pollution on S1 and S6 station was either of petrogenic origin or pollution of more recent dates. The highest contribution of HMPAH fraction was observed on S3 station (67,1%) and S2 station (59%) whereas the lowest HMPAH contribution was observed on S6 station. (15,2%) On other investigated station, HMPAH were dominant PAH compounds in the mixture contributing to total PAH concentration with more than 40%. PAH fingerprint pattern with the dominance of HMPAH is typical for the industrialized and urbanized coastal areas where intense anthropogenic pressures are present (WAKEHAM *et al.*, 1996; BENLACHEN *et al.*, 1997; STORELLI & MARCOTRIGIANO, 2000). The dominance of this fraction in the open sea sediments is more likely caused by greater persistence of HMPAH to degradation, causing sediment enrichment with heavier PAH compounds during the time. Relative contributions of 6-ring PAH fractions were higher in the open sea sediments with the maximum value determined on S5 station, where 21,7% of total PAH concen-

tration were ascribed to 6-ring PAH. Relatively high contributions of this fraction were also observed on S7 (19,6%) and S8 station (17,4%). In Kaštela Bay, contributions of 6-rings fraction was the lowest: only 2,9% of total PAH concentration were ascribed to this fraction on S1 station and 7% on S2 station. Six-rings PAH are the heaviest PAH fraction investigated in this study and is typically formed during the high-temperature combustion (GSCHWEND & HITES, 1981; KIM *et al.*, 2008; LUO *et al.*, 2008, ELMQUIST *et al.*, 2007; LEHNDORF & SCHWARK, 2009). During the crude oil distillation, 6-ring PAH will be present in the heavier fractions such as diesel fuel, heating oil and distillation resins that are typically used for ship fuels, therefore this fraction was suspected to originate from a fuel combustion in ship engines or from accidental fuel spillage on the sea surface (STOUT & WANG, 2007).

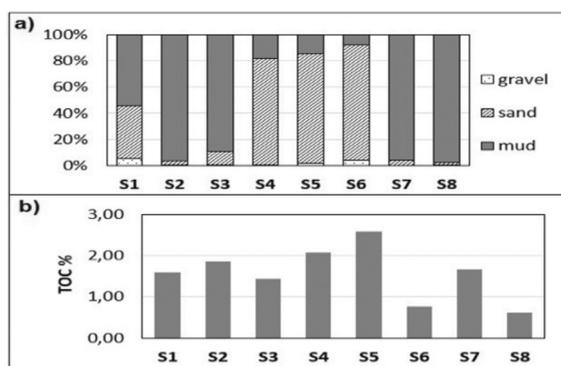


Fig. 6. Grain-size distribution and total organic carbon (TOC) in the sediments of the investigated stations

### Polycyclic aromatic hydrocarbons in relation to sediment particle size and total organic carbon

Grain-size distribution of sediment and total organic carbon (TOC) of investigated sediments are shown in Fig. 6.

Gravel content, ranging from 0% (S7) to 5,6% (S1), was the least abundant size fraction in sediments. Somewhat higher amounts of gravel were found on S5 (1,68) and S6 (3,91) while on the other stations, gravel amount was lower than 1% (Fig. 6a). Sand particles were dominant in sediments of S4, S5 and S6 sta-

tion while on the other investigated stations dominant sediment fraction was mud. Coastal stations typically contain a higher amount of fine fraction, mainly due to the Jadro River inputs of fine grain material originating from the land. Anthropogenic activities also contribute to increased level of fine particles in sediments. These results are in good accordance with previous research studies conducted in Kaštela Bay (BOGNER & MATIJEVIĆ, 2016) and other regions of the Adriatic Sea, where higher amounts of mud particles were usually observed in the coastal region. The high amount of muddy particles in the sediments of S7 (95,97%) and S8 stations (97,72%) is probably due to riverine inputs of fine grain materials. These two stations are nearest to the western Adriatic coast and nearest to the Po River delta. Rivers of the Po valley are known for introducing high amounts of land-based material, which is further spread, by the sea currents. This material is enriched with the fine size particles and consequently influences grain size distribution and sediment properties in the western Adriatic (RAVIAOLI *et al.*, 2008; BOGNER & MATIJEVIĆ, 2016). The sand fraction was dominant on S4 (81,10%), S5(83,74%) and S6 (87,92%) which are the most remote stations from the coast. Open-sea sediments contain smaller amount of fine grain particles due to the greater distance from riverine inputs and anthropogenic pressures. Sediment in the open-sea regions was enriched with sandy fraction, which is partly a natural state of the open sea sediments and the erosion of the nearby islands further contributed to it (RAVIAOLI *et al.*, 2008; BOGNER & MATIJEVIĆ, 2016).

TOC values were higher in the open sea sediments (Fig. 6b) than in the coastal zone. Maximum TOC value was observed on S5 station (2,59%) whereas the lowest PAH values were measured on S8 station. TOC values were not correlated with determined PAH concentration since higher TOC values were observed in the open sea sediments where PAH concentrations were the lowest. If low TOC value on the S8 station was observed along with the perylene concentration, it can be assumed that enhanced biological activity in the sediment results in

greater biological uptake of organic carbon for the biosynthesis causing lower TOC content of the sediment (PAGE *et al.*, 1996; TOLOSA *et al.*, 2004). Absent correlation between PAH concentrations and TOC in sediments could be ascribed to their different origin since TOC is a natural component of the sediment, whereas most of the PAHs are of anthropogenic origin.

### Assessment of PAH origin by application of diagnostic ratios

Concentration ratios of PHE/ANT, FLY/PY, BaA/CHR, IP/BPER, calculated for the investigated samples are shown in the form of double concentration plots in Fig. 7.

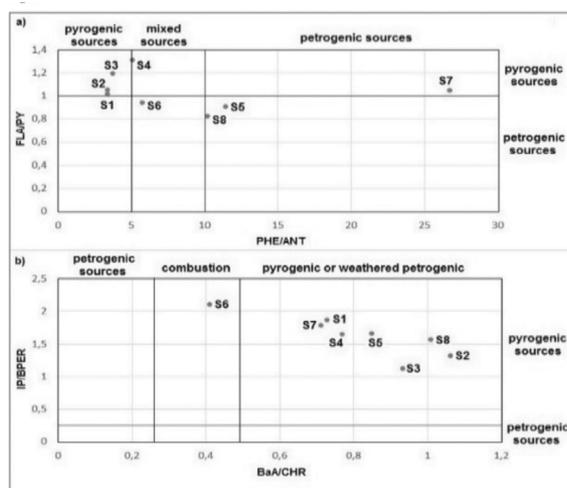


Fig. 7. Concentration ratios PHE/ANT, FLY/PY, BaA/CHR, IP/BPER presented as a double plots of a) PHE/ANT vs FLY/PY, b) BaA/CHR vs IP/BPER

Phenanthrene, as the most stable 3-rings PAH, is produced during the conversion of organic matter in petroleum components and its prevalence over anthracene is commonly considered as an indicator of petrogenic pollution (GOGOU *et al.*, 2000; DE LUCA *et al.*, 2004; LIMA *et al.*, 2005). Therefore, low values of PHE/ANT ratio are more likely for the combustion process, whereas high ratio values indicate petrogenic pollution. Ratio values calculated for the sediments of S5 (11,44), S7 (26,72) and S8 (10,18) station indicated the dominance of petrogenic sources. In sediments on S1, S2 and S3 stations, low PHE/ANT ratios of 3,36 (S1), 3,37 (S2) and

3,71 (S3) corresponded with pyrogenic sources whereas on the S4 and S6 station ratio values indicated equal contributions of both, petrogenic and pyrogenic sources. Stations S1, S2 and S3 being situated in the coastal area are more influenced by industrial and urban activities than other investigated stations, thus, sediment enrichment with anthracene can be ascribed to the combustion process. On the rest of the investigated stations, contribution of petrogenic sources was greater, especially on the S7 station where ratio value of 26,72 strongly suggest petrogenic pollution.

FLA/PY ratio is also thermodynamically derived ratio commonly applied to distinguish between different PAH sources. Fluoranthene, as a less stable isomer, is preferably formed during the high-temperature process while on the contrary, pyrene is suspected to be the product of petrogenesis (SICRE *et al.*, 1987; BUDZINSKI *et al.*, 1997). Therefore, low FLA/PY ratio (<1) are commonly attributed to pyrogenic sources and ratios higher than 1 to the petrogenic sources. When applied, these criteria suggest petrogenic source of pollution in sediments on S5 (0,91), S6 (0,94) and S8 (0,86) station whereas on the other investigated stations, FLA/PY ratio indicates the pyrogenic origin of PAH. If these results are compared to those obtained by application of PHE/ANT ratio it is seen that result for S1, S2, S3, S4, S5 and S8 stations overlap with the result of PHE/ANT ratios while on the rest of the investigated stations slightly different results are observed.

BaA/CHR ratio values were within the 0,41 (S6) and 1,06 (S2) range. During the combustion process, BaA is preferentially produced over chrysene, which enables differentiation between petrogenic and pyrogenic sources (YUNKER *et al.*, 2002; DE LUCA *et al.*, 2004). Criteria adopted in this study were as follows: BaA/CHR < 0,25 indicated petrogenic sources, 0,25 < BaA/CHR < 0,5 is for petroleum combustion and BaA/CHR > 0,5 indicated other combustion processes (YUNKER *et al.*, 2002). According to this, PAH mixtures in all samples originate from pyrogenic sources. De Luca proposed higher transition point from petrogenesis to pyrogenesis, suggesting that

BaA/CHR ratio  $<1$  indicate petrogenesis while ratios  $>1$  indicate pyrogenesis (DE LUCA *et al.*, 2004). When this suggestion was taken into consideration it can be concluded that PAH mixtures in sediment at the majority of investigated stations are petroleum derived, except for S2 and S8 station, where ratio values of 1,06 and 1,01 indicated the pyrogenic origin of PAH. Results derived by application of BaA/CHR ratio differ from the previously obtained results. These differences can be ascribed to the different behavior of PAH compounds during the weathering. BaA is more suspected to the process of photolysis and shows different environmental behavior than CHR (YUNKER *et al.*, 2002; TOBISZEWSKI & NAMIESNIK, 2012). As a less stable isomer, BaA converts to Chrysene during degradation, reducing the ratio value; therefore, caution has to be applied when using this ratio for weathered pollution (SOCLO *et al.*, 2000; YUNKER *et al.*, 2002; STOUT *et al.*, 2003).

IP/BPER ratio indicated pyrogenic sources of PAH in sediment samples of each investigated station. Inconsistency of the result obtained by application of this ratio with three previously applied criteria is probably due to the different behavior of these two PAHs in the atmosphere. Atmospheric degradation of these isomers is highly influenced by the particle association: degradation rates are the same for both isomers when attached on black particles whereas IP degrades faster than BPER when attached to gray particles and much slower when attached to white particles (BEHYMER & HITES, 1998).

Concentration ratios between following pairs of compounds: C1-PHE and PHE; C1-PY and PY; CHR and C2-CHR and C-PAH/PAH, are shown in Fig. 8. Phenanthrene will dominate over its methyl-homologues in PAH mixture formed during the combustion (LEHNDORF & SCHWARK, 2009); although, combustion at low temperature also preserves petrogenic alkylation pattern. Some petrogenic sources, such as petroleum oil shales and their refined products may also obtain C1-PHE/PHE ratio values higher the two (GSCHWEND & HITES, 1981; KIM *et al.*, 2008; LUO *et al.*, 2008). When C1-PHE/PHE value is smaller than one, pyrogenic sources are more likely (ELMQUIST *et al.*, 2007). Heavy petroleum

fractions, such as creosote and coal tar also show low C1-PHE/PHE ratio ( $< 0,2$ ) while ratios values 1-2 correspond to both, petrogenic and pyrogenic sources, and can be ascribed to coal, automobile exhaust, motor oils and used lubricants (ELMQUIST *et al.*, 2007). In this study, C1-PHE/PHE ratios  $< 0,2$  are ascribed to coal tar and creosote; values in the range 0,2-1 to pyrogenic sources; values 1-1,5 to mixed sources while ratios higher than 1,5 were ascribed to unburned petroleum (Fig. 8a). According to this ratio, combustion was the dominant source of PAH in sediments at S3 (0,82) station while unburned petroleum was dominant PAH source on following stations: S5 (1,53), S6 (1,65), S7 (1,77) and S8 (2,66). Mixed sources were identified on S1, S2 and S4 station.

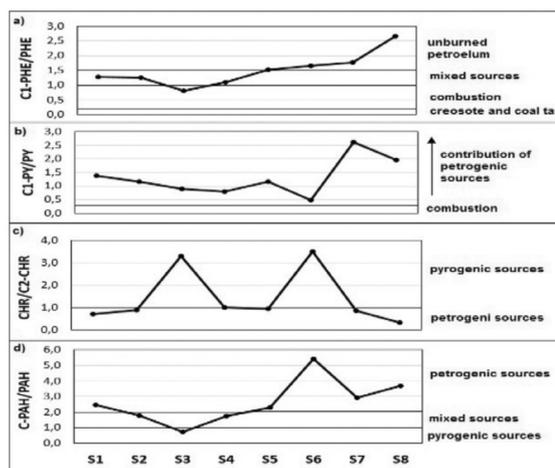


Fig. 8. Concentration ratios of: a) C1-PHE and PHE b) C1-PY and PY, c) CHR and C2-CHR d) total alkyl-substituted total PAHs and PAHs; in the investigated samples

Low C1-PY/PY ratio values indicate pyrogenic source while higher values indicate petrogenic source of pollution. Higher the ratio, contribution of the petrogenic sources is higher (BUCHELI *et al.*, 2004). When applied, this ratio values showed the greatest contribution of pyrogenic sources on the S6 station (Fig. 8b) while unburned petroleum is the most likely source of pollution on S7 station. Ratio values corresponding with petrogenic sources were also observed on the S8 (1,98) and S1 (1,37) station while on the rest of the investigated stations pyrogenic sources were the main source of PAH pollution.

PAH mixtures emitted from pyrogenic sources typically show CHR/C2-CHR ratios higher than one whereas low ratio values (<1) indicate petrogenic pollution (STOUT *et al.*, 2004). According to this ratio, petrogenic sources are dominant on the most of the investigated station (Fig. 8c), except for S3 and S6 station where high ratio values (>3) strongly suggest the dominance of pyrogenic sources. Another indicator based on chrysene and alkyl-chrysene concentrations is a relation between concentrations of chrysene and its alkyl-isomers. In mixtures formed during the combustion, chrysene concentrations are higher than C1-chrysene and tend to decrease as the degree of alkylation increase. Thus, in case  $CHR > C1-CHR > C2-CHR > C3-CHR > C4-CHR$ , PAH are considered to be of pyrogenic origin while on the contrary, if the concentration of any methylated chrysene group is higher than a concentration of parent chrysene, the dominance of petrogenic sources is indicated (WANG *et al.*, 1999b). These criteria confirmed results provided by CHR/C2-CHR ratio: PAH mixtures on S3 and S6 stations are mainly from pyrogenic sources while on the other station domination of petrogenic sources is observed (Table 3).

C-PAH/PAH ratio was successfully applied in order to discriminate between petrogenic and pyrogenic sources of PAH pollution over large geographic areas and during the long timespans (YAN *et al.*, 2006). It was shown that pyrogenic sources produce PAH mixtures with low ratio values, lower than one, respectively. Petroleum combustion yields the highest ratio value of 1.1 and it is an upper limit for the pyrogenic sources, whereas coal combustion produces mixtures with a ratio value of 0,35 (YAN *et al.*, 2007). PAH compounds taken into account for this ratio were PAH with molecular masses of 128, 178, 202 and 228, respectively. Ratio values for the investigated sediments indicated the dominance of pyrogenic sources only on S3 station (Fig. 8d). The petrogenic source of pollution were the most important PAH sources on S1, S5, S6, S7 and S8 station while on the S2 and S4 station equal contribution of petrogenic and pyrogenic sources was determined (Fig. 8d).

The pyrogenic index is the ratio of the sum of the concentrations of unsubstituted 3-6 PAHs,

enlisted on EPA 16 priority list, to the sum of the concentration of the five alkylated homologues: naphthalenes, fluorenes, dibenzotiphenes, phenanthrenes and chrysenes (WANG *et al.*, 1999b). PI values are higher for pyrogenic sources whereas low PI values indicate petrogenic pollution. According to this ratio (Fig. 9.), PAH mixtures on S3 were of pyrogenic origin while on the other investigated station, prevalence of petrogenic sources was observed, especially on S1, S6 and S7 station where index values were as follows: 0,28 (S1), 0,18 (S6) and 0,54 (S7).

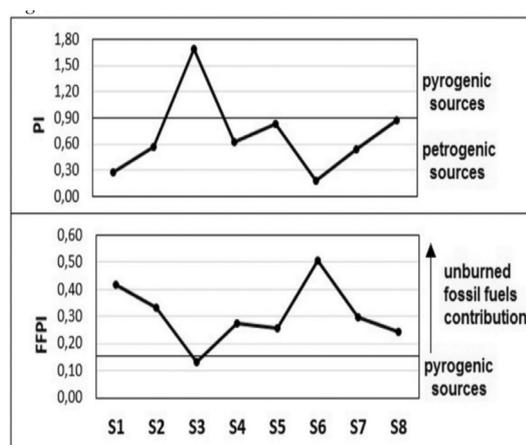


Fig. 9. Pyrogenic index (PI) and fossil fuel pollution index (FFPI) determined in the investigated samples

FFPI was the last index used for PAH source apportionments. Index values close to zero correspond with the most pyrogenic PAH mixtures while for the unburned fossil fuel this value is close to one (IQBAL *et al.*, 2008). Petrogenic sources contribution to overall PAH concentration increase as the index value increases. FFPI index indicated the dominance of pyrogenic sources only on S3 station. High petrogenic PAH contributions were observed on S1 and S6 station while on the other investigated station index values showed a slightly higher contribution of petrogenic sources over pyrogenic ones.

## CONCLUSIONS

Total PAC concentrations in the investigated area ranged from 39,93 (S4) to 2663,27 (S1). PAHs were a dominant group on each station contributing to the total PAC concentration with

more than 85%. Parent PAH compounds were found to be dominant PAH fraction only on S3 station. Total concentrations of both, PAC and PAH, decreased as the distance from the coast increased, reaching minimum value on S4 station. Absolute concentrations of heterocyclic aromatic compounds also decreased as the distance from the coast increased, but contributions of O-PAHs in total PAC concentrations increased with the distance, being highest in the open sea sediments. This was mainly ascribed to the biologically mediated conversion of PAH into O-PAH during the degradation and it was probably further contributed by transportation of O-PAH from coastal zone. In the most of investigated stations, BFL and C1-302 were dominant PAH compounds, although dominance of methyl-PAH was observed at all station except for S3. Marine traffic was suspected to be the most likely reason for BFL dominance in the open sea sediments since BFL are emitted in large amounts during the fuel combustion in engines. The C1-302 fraction is also suspected to be transportation-derived as this fraction is the heaviest product of petroleum distillation commonly used as ship fuel. Due to the high molecular weight, C1-302 fraction is the least degradable one implying that sediments will be enriched with this fraction since the concentrations of the lighter PAH compounds tend to decrease due to degradation. The high amount of perylene measured on S8 station suggests enhanced biological activity at this location. Grain-size analyses showed that fine, muddy particles were dominant sediment fraction in coastal areas whereas in the open sea area sediments were enriched in sandy fraction. These findings are in good accordance with other research in which coastal sediments contain an elevated amount of muddy particles due to the

riverine input of land-based materials. Sediment grain-size distribution determined in this study is also in good accordance with results of previous research studies on sediments of the Adriatic Sea. Although PAH concentrations were higher in the sediments with enhanced amount of fine particles, this cannot be ascribed to differences in mud content as the intense activities in the coastal zone are more likely responsible for elevated PAH concentrations. Diagnostic ratios strongly suggest petrogenic origin on S1, S5, S7, and S8 station where the petrogenic origin was indicated by six or more applied criteria. Pyrogenic origin was determined only on S3 station where 10 out of 11 applied criteria corresponded to pyrogenic sources. Equal contribution of both, petrogenic and pyrogenic sources was determined on S2, S4 and S6 station. Data presented here are preliminary results of more complex research of polycyclic aromatic compounds in the Adriatic Sea. Additional investigations on PAH origin, sediment properties, toxicity and seasonal changes in PAH concentrations will be presented in the future papers.

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## Koncentracije i porijeklo policikličkih aromatskih ugljikovodika u sedimentima srednjeg Jadrana

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### SAŽETAK

Policiklički aromatski spojevi (PAC) i njihovi supstituirani homolozi su istraživani u sedimentu na osam postaja smještenih uzduž transekta Hrvatska-Italija, u srednjem Jadranu. U svakom uzorku određeno je ukupno 208 spojeva. PAC koncentracije, izmjerene u sedimentima u priobalnom području, bile su više od PAC koncentracija izmjerenih u sedimentima otvorenog mora. Najviša koncentracija izmjerena je u području teretne luke Split. Policiklički aromatski ugljikovodici (PAH) bili su dominantna grupa spojeva u svim istraživanim uzorcima s udjelima u ukupnoj koncentraciji PAC-ova višim od 85%. Maseni udjeli S-PAH-ova bili su viši od masenih udjela O-PAH-ova u svim uzorcima te su opadali udaljavanjem od obale. Doprinosi O-PAH u ukupnom masenom udjelu PAC-ova povećavao se udaljavanjem od obale dok su doprinosi S-PAH bili viši u priobalnom području što upućuje na njihovo različito porijeklo. Granulometrijskom analizom sedimenta utvrđeno je da su sedimenti u priobalnom području sadržavali povišeni udio finih, muljevitih čestica dok su čestice veličine pijeska bile dominantna frakcija u sedimentima otvorenog mora. Udjeli ukupnog organskog ugljika (TOC) bili su niži u sedimentima uz obalu gdje su izmjereni povišeni maseni udjeli PAC-ova što upućuje na njihovo različito porijeklo. Izvori PAH-ova istraženi su primjenom dijagnostičkih omjera. Pirogeno porijeklo PAH-ova određeno je na samo jednoj postaji, smještenoj u priobalju, dok su na postajama otvorenog mora dominirali PAH-ovi iz petrogenih izvora. Rezultati upućuju da je pomorski promet glavni izvor onečišćenja u području otvorenog mora.

**Ključne riječi:** policiklički aromatski spojevi, PAH-ovi, sediment, porijeklo PAH-ova, dijagnostički omjeri, onečišćenje mora, Jadransko more