

Assessment of environmental risk related to the polycyclic aromatic hydrocarbons (PAH) in the sediments along the eastern Adriatic coast

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Polycyclic aromatic hydrocarbons (PAH) were investigated in the sediments at 24 locations in the coastal area of Adriatic Sea. Total PAH concentrations ranged from 14,98 to 26145,62 µg kg⁻¹, with the highest levels determined in the sediments of Šibenik Bay and the lowest in the sediment near Island of Pag. Unsubstituted PAH were prevailing PAH group in the sediments from the Šibenik Bay and in the Coastal area, while methyl-substituted PAH were dominant group in the sediments of the Kaštela Bay. In order to estimate the possible toxicological significance of PAH concentrations, Sediment Quality Assessment was done according to three different sets of sediment quality guidelines. A high environmental risk was calculated for each station in Šibenik Bay; for the station in vicinity of the Industrial port of Split and for the two stations in Coastal zone. Low environmental risk was determined in less urbanised areas such as Island of Pag. Sediment extracts were further analysed for acute toxicity by measurements of decrease in bioluminescence upon exposure to sediment extracts. Obtained results show disagreement between sediment toxicity predicted upon PAH levels in sediment and experimentally obtained sediment toxicity. Sediment extracts in which low PAH levels were measured showed high acute toxicity indicating that concentrations of PAH alone are a poor indicator of sediment toxicity. Correlation analysis between concentrations of specific PAH compounds and toxicity revealed the strongest association between acute sediment toxicity and sulphur-containing PAH suggesting the S-PAH should be considered in sediment toxicity assessment.

Key words: PAH; sediment; Adriatic Sea; sediment quality assessment; bioassay; marine pollution

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are subclass of polycyclic aromatic compounds consisting of two or more fused aromatic rings in their structure (VOLHARDT, 1999). As products of incomplete combustion of coal, fuel, biomass and other organic materials, PAH in the environment originate from numerous anthropogenic activities: Traffic and transportation, power plants, industrial furnaces, waste incineration, coke production, asphalt and petroleum cracking (NEFF, 1979). When released into the environment, PAH enter marine systems through atmospheric deposition, riverine inputs, urban runoff and accidental oil spillages (TSAPAKIS *et al.*, 2003). Due to the high hydrophobicity, PAHs tend to adsorb to particulate organic matter and sink through the water column before settling in bottom sediment (TSAPAKIS *et al.*, 2003; NEFF, 1979) where they can persist toward degradation for long periods causing adverse effects for marine organisms. Being highly carcinogenic and mutagenic, with disrupting effects on lymphatic system and hematopoietic activity (ATSDR, 1990b., SANTODONTO & BASU, 1981). PAH have been subject of many environmental researches, while risk they pose to the aquatic organisms is recognized by international organisations and conventions that aim to protect environmental and human health. The most important include the Barcelona Convention for the Protection of the Mediterranean Sea, Mediterranean Marine Pollution Monitoring and Research program (MedPol) and Mediterranean Action Plan (MAP). European directives such as the Water Framework Directive and the Marine Strategy Framework Directive (2008/105/EC) enlisted PAH as priority pollutants. US Environmental Protection Agency incorporated 16 PAHs to a priority pollutant list to be monitored in the environment (USEPA, 1980).

The composition of PAH mixtures emitted into the environment is source-specific and thus, show different toxicological profiles (NEFF, 1979; ATSDR, 1990b). Mixtures derived from unburned fossil fuels are enriched in alkylated, low molecular weight PAHs, while PAH mixtures resulting

from combustion processes typically contain a high amount of unsubstituted, heavier PAH compounds. Toxicity to aquatic organisms also depends on the structure of the specific PAH compound as well as the exact specie of the marine organism (ATSDR, 1990b; YUNKER *et al.*, 2002; STOUT & GRAAN, 2010). It is generally observed that bivalves and other filter feeders accumulate greater amounts of low molecular weight PAH compared to heavier PAH as this fraction is more soluble in the seawater and thus more bioavailable for accumulation in marine organisms (DE GIOVANNI *et al.*, 2022). In addition, PAH compounds with high molecular weight and 4 or more rings in their structure can be metabolised and excreted from the organism resulting in a low bioaccumulation rate. However, this heavier PAH fraction can mimic primary nucleobases, such as cytosine and guanine, and incorporate into the human DNA structure, leading to cell damage, mutagenesis and tumour formation (SANTODONTO & BASU, 1981; ATSDR, 1990b). In the recent work of De Giovanni *et al.* a database on the concentrations of PAH in Mediterranean seafood was compiled based on the research results of several studies on the accumulation of PAH in different marine organisms. In the tissues of the studied organisms from the Adriatic Sea, the predominant PAH compound was phenanthrene, which can be attributed to the better solubility and bioavailability of low molecular weight PAH, as well as to the faster metabolism of the heavier PAH compounds (DE GIOVANNI *et al.*, 2022). The calculation of two health risk indices (excess lifetime cancer risk and target hazard quotient) showed that PAH concentrations in the studied organisms posed minimal risk for environmental health. It was also shown that PAH concentrations show trend of increase in the studied organisms, highlighting the need for continuous monitoring (DE GIOVANNI *et al.*, 2022).

In order to assess biological relevance of PAH concentrations in the environment, sediment quality guidelines (SQG) have been developed by many environmental protection agencies and governmental agencies. These guidelines were empirically derived upon the databases of PAH

concentrations that coincide with occurrence of harmful effects on aquatic organisms and are widely used in sediment quality assessment. However, these guidelines differ among each other according to the concentration levels that coincide with occurrence of harmful effects, whereas, some differ among each other according to the different PAH compounds that were taken for consideration and toxicity evaluation (LONG *et al.*, 1995; MACDONALD *et al.*, 2000).

While sediment quality assessment is based on the observed biological effect that coincide with concentration of particular PAH compound in the sediment, determination of acute toxicity of sediment extracts by bioassays can be performed to test acute PAH-related toxicity of the sediment.

In this study, PAH related sediment quality in the coastal zone of eastern Adriatic was assessed by application of SQGs that were proposed by: National Oceanic and Atmosphere Association (NOAA), Canadian Council of Minister (CCME) and OSPAR Commission (NOAA, 1998; CCME, 2001; OSPAR, 2004). Furthermore, acute toxicity measurements of sediments extracts were performed by application of bioassays. Results obtained by different methods for PAH-related sediment toxicity evaluation were combined and compared in order to suggest best approach for prediction of PAH-related environmental risk in Adriatic Sea. The focus of this study was sediment toxicity assessment and evaluation of different sets of SQGs, whereas PAH levels and sources in the sediments of Adriatic Sea have been thoroughly discussed in the previous paper (MANDIĆ *et al.*, 2018).

MATERIAL AND METHODS

Study area

The research area covers the eastern Adriatic coast from the island of Pag in the north to the city of Dubrovnik in the south, as shown in Fig. 1. These areas are located in urban areas or in areas under the influence of inland traffic and/or maritime activities. Twelve stations in the coastal zone were selected for this study: near the

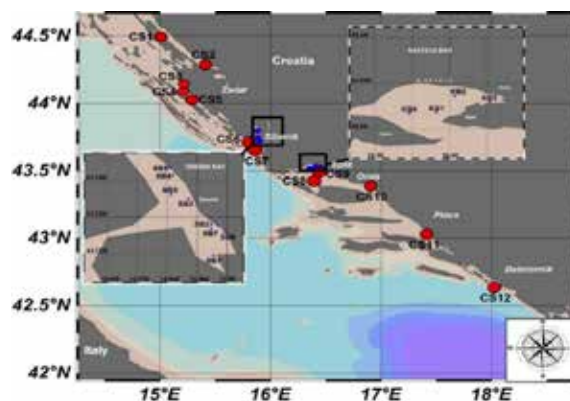


Fig. 1. Research area encompassing 12 coastal stations situated from Island of Pag to City of Dubrovnik; 4 stations in the Bay of Kaštela and 8 stations in the Bay of Šibenik (MANDIĆ *et al.*, 2018.)

island of Pag, in the Velebit Channel, near the city of Zadar and the port of Zadar (Gaženica), near Biograd, Šibenik, Split, Omiš, Ploče and Dubrovnik. Two areas in the coastal zone, which were heavily industrialised throughout history, were selected for more detailed study: Kaštela and the Bay of Šibenik, respectively (Fig. 1).

Kaštela Bay is the largest bay in the central Adriatic with an area of about 60 km². It is influenced by the fresh water supply of the river Jadro in the north-eastern part, which decreases the salinity compared to the open sea regions. This area is strongly affected by industrial activities such as cement production, shipyards, industrial ports and urban activities in the surrounding cities (ANDELIĆ *et al.*, 2015). Coastline area of the Kaštela Bay was heavily industrialised throughout the past, but industrial activities were mostly abounded with simultaneous development of maritime transport and nautical tourism.

Šibenik Bay, with an area of 4 km², is an estuary of the Krka River and thus an important habitat. It is a saline estuary with a stratified water column connected to the coastal zone by a shallow channel. This semi-enclosed area has limited water circulation that varies seasonally due to freshwater discharge rates and very low water exchange rates of the bottom marine waters with the outer coastal waters (BUŽANČIĆ *et al.*, 2015; MANDIĆ *et al.*, 2018). Similar to Kaštela Bay, Šibenik Bay was also heavily industrial-

Table 1. List of analysed PAH compounds and abbreviations used in the text

COMPOUND NAME	ABBREVIATION	COMPOUND NAME	ABBREVIATION
PAH			
Naphtalene	N	Benzo[<i>a</i>]pyrene	BaP
C1-Naphtalenes	C1-N	Benzo[<i>e</i>]pyrene	BeP
C2-Naphtalenes	C2-N	Perylene	PER
C3-Naphtalenes	C3-N	Dibenzo[<i>a,e</i>]pyrene	DBP
C4-Naphtalenes	C4-N	Benzo[<i>b+j</i>]fluoranthene	BbjFL
ΣC-Naphtalenes	C-N	Benzo[<i>k</i>]fluoranthene	BkFL
Acenaphtene	ACE	C1-Benzofluoranthenes	C-BFL
Acenaphtylene	ACY	Benzo[<i>ghi</i>]perylene	BghiP
Fluorene	F	Dibenzo[<i>a,h</i>]anthracene	DBA
C1-Fluorenes	C1-F	Indeno[<i>1,2,3-cd</i>]pyrene	IP
C2-Fluorenes	C2-F	Coronene	COR
ΣC-Fluorenes	C-F	S-PAH	
Anthracene	ANT	Dibenzothiophenes	DBT
Phenanthrene	PHE	C1-Dibenzothiophenes	C1-DBT
C1- Phenanthrene	C1-PHE	C2-Dibenzothiophenes,	C2-DBT
C2- Phenanthrene	C2-PHE	ΣC-Dibenzothiophenes	
C3- Phenanthrene	C3-PHE	Benzo[<i>b</i>]naphthothiophenes	BNT
ΣC-Phenathrenes	C-PHE	C1- Benzo[<i>b</i>]naphthothiophenes	C1-BNT
Fluoranthene	FLA	O-PAH	
Pyrene	P	Dibenzo[<i>b,d</i>]furan	DBF
C1-Pyrenes	C1-P	C1 - Dibenzo[<i>b,d</i>]furan	C1-DBF
C2-Pyrenes	C2-P	C2 - Dibenzo[<i>b,d</i>]furan	C2-DBF
ΣC-Pyrenes	C-P	ΣC-dibenzo[<i>b,d</i>]furanes	C-DBF
Benzo[<i>a</i>]anthracene	BaA		
Chrysene	CHR		
C1-Chrysene	C1-CHR		
C2-Chrysene	C2-CHR		
C3-Chrysene	C3-CHR		
ΣC-Chrysenes	C-CHR		

ised, with ferroalloy plants, alumina production plants and plastic factories being the most important. In the last three decades, industrial activities were abounded but urban pressures and maritime activities have increased due to the development of nautical tourism and aquaculture.

Sediment samples were collected at most of the stations during the winter (February/March) of 2013, except at stations SB6, SB7, and SB8, where sediment samples were collected during October of 2013. Additional information for

each station is given in the Table 1. of Supplementary Information (SI).

Qualitative and quantitative analyses of polycyclic aromatic hydrocarbons

Polycyclic aromatic compounds were determined according to the method developed by IFREMÉR laboratories (TRONCZYNSKI et al., 2004). In brief, sediment samples were weighed into the extraction cell upon which internal standard solution containing two deuterated PAH compounds (Phenanthrene-d10 and Benzo[*e*]pyrene-d12) were added to the sample.

Extraction was performed by ACE (Accelerated solvent extractor) with dichloromethane (DCM) as a solvent, under 100°C and 138 Bar. Sediment extracts were evaporated in a rotary evaporator and further concentrated under gentle nitrogen steam up to the volume of 1 ml. Cleaning and fractionation were obtained by the means of column chromatography with SiO₂ and Al₂O₃ as sorbents. 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. All three fractions were joint together, evaporated in the rotary evaporator and concentrated under nitrogen steam. Sediment extracts were analysed 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 µm) in On-column injection mode. List of analysed PAH compounds and abbreviations used in text is given in the Table 2., while list of all analysed compounds, with the molecular weight and internal standard used as a reference, are given as Table 2 of SI. Quality control and quality assurance were achieved by usage of laboratory and field blanks, surrogate standards and standard reference materials. (SRM 1491 and SRM 2977) obtained from the National Institute of Standards and Technology-NIST Samples with recoveries below 70% were rejected and reanalysed (MANDIĆ *et al.*, 2018).

Based on the different structure, properties and toxicity, the investigated PAH compounds were divided into six characteristic groups and further discussed as such:

- a) T-PAH – sum of all investigated PAH compounds;
- b) parent-PAH – sum of non-alkylated, unsubstituted PAH compounds: N, ACE, ACY, F, ANT, PHE, FLA, P, BaA, CHR, BaP, BeP, PER, DBP, BbjFL, BkFL, BghiP, DBA, IP and COR.
- c) 16-EPA PAH – 16 PAH compounds listed as high priority pollutants by EPA: N, ACE, ACY, F, ANT, PHE, P, FLA, P, BaA, CHR, BbjFL, BkFL, BaP, IP and BghiP;
- d) Me-PAH - sum of mono-, di-, tri- and

tetra- methyl substituted compounds: C-N, C-F, C-PHE, C-P, C-CHR and C-BFL;

e) S-PAH – sum of sulphur-containing PAH compounds: DBT, C-DBT, BNT and C1-BNT;

f) O-PAH – sum of oxygen-containing PAH compounds: DBF and C-DBF.

Sediment Quality Assessment

Sediment quality guidelines (SQGs) for sediment quality assessment (SQA) have been developed over the past two decades in order to be used to predict adverse biological effects. These guidelines were developed according to the Biological Effects Database for Sediment (BEDS), which contains concentration data linked with co-occurring adverse biological effects. The most widely used SQG are those developed by NOAA and those that were developed upon recommendations of CCME (MACDONALD *et al.*, 2000; CCME, 2001; LONG *et al.*, 2015).

These two sets of SQGs take into consideration the same PAH compounds, although levels of concerns are much lower in the case of CCME. This difference is due to the different databases used for their development. CCME guidelines were developed upon much larger database and thus considered more accurate in sediment toxicity predictions (MACDONALD *et al.*, 2000; CCME, 2001; LONG *et al.*, 2015).

NOAA system distinguishes two concentration levels: Effect Range Low (ERL), which is the concentration below which adverse effects rarely occur; and Effect Range Median (ERM), which is the concentration above which adverse effect frequently occur. The concentration levels between ERL and ERM are considered as a concentration range within which adverse biological effects occasionally occurs. In the case of CCME, two concentrations levels are also recommended: Threshold Effect Level (TEL) and Probable Effect Level (PEL) that correspond with ERL and ERM values, respectively (NOAA, 1998).

In this work, environmental risk was assessed by application of yet another SQGs developed by the OSPAR Commission for North Atlantic sediments (OSPAR, 2004). These SQGs consider

different compounds than NOAA and CCME while also differ two concentration levels: Background Assessment Concentration (BAC) and Effect Range Low (ERL). These two values also correspond to ERL/ERM and TEL/PEL set of values with BAC corresponding to the concentration level below which adverse effects rarely occur and ERL corresponding to the concentration level above which adverse effects frequently occur.

Acute toxicity of sediment extracts

The acute toxicity of sediment extracts was investigated using a specially developed bioassay - Microtox®. (BIHARI *et al.*, 1989 ; BIHARI *et al.*, 2006; FERNANDEZ-PINAS *et al.*, 2014). The toxicity of the sediment extracts was determined by the decrease in bioluminescence of *Vibrio fischeri* bacteria after exposure to sediment extracts. The test was performed using the Microtox® test DIN EN ISO 11348-3 Biofix®, while the decrease in bioluminescence of the bacteria was measured using the Monolight 2010 Illuminometer (BIHARI *et al.*, 1989; BIHARI *et al.*, 2006). The LD50, which is the amount of sediment extract that causes a 50% decrease in initial bacterial bioluminescence, was multiplied by 1000 and the reciprocal values were used to study toxicity, as shown in the following equation:

$$TOXICITY = \frac{1}{LD50 \cdot 1000}$$

where LD50 is a quantity of sediment extract that caused 50% decreased of initial bacterial luminescence.

Table 2. Sediment status according to the result of sediment toxicity assay

Toxicity (1/LD50*1000)	Sediment Status
<5	EXCELLENT
5-20	GOOD
20 - 100	POOR
>100	VERY POOR

RESULTS AND DISCUSSION

PAH concentrations in the sediments

Concentrations of specific groups of PAH compounds in the sediment of Coastal area are shown in Fig. 2.

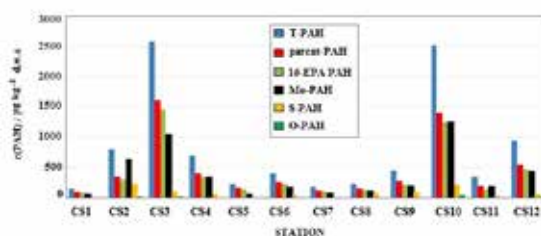


Fig. 2. Concentration of total PAH (T-PAH), 16 EPA priority PAH (16 EPA PAH), unsubstituted PAH (parent-PAH), methyl substituted PAH (Me-PAH), sulphur containing PAH (S-PAH), and oxygen containing PAH (O-PAH) at studied stations in the Coastal zone

The highest T-PAH concentrations in the coastal area were measured at station CS3 near the town of Zadar (2639,55 µg kg⁻¹) and at station CS10 in front of the former chromium alloy factory, near the town of Omiš, where T-PAH concentration of 2643,48 µg kg⁻¹ was measured. In the sediment of CS3 station, the concentration of 16 EPA PAH contributed with more than 50% to the T-PAH concentration. Concentrations of parent PAH were higher than concentrations of Me-PAH indicating that combustion processes were the main source of PAH pollution on this location (NEFF, 1979; DE LUCA *et al.*, 2000; WITT, 2002; PONCE-VELEZ *et al.*, 2006) T-PAH concentration and composition of PAH mixture determined at this location are similar to the concentrations reported for other urbanised locations where dominant PAH sources, such as residential heating, municipal runoffs and traffic, contribute to elevated concentrations of unsubstituted, parent PAH compounds (NEFF, 1979; SOCLO *et al.*, 2000; WITT, 2002; PONCE-VELEZ *et al.*, 2006). At station CS10, the predominance of parent-PAH compounds is not as pronounced as observed at CS3. Station CS10 is located near the former ferrochromium factory where coke was used as fuel for combustion in

high furnaces. Since combustion processes produce mixtures enriched in unsubstituted, high molecular weight PAH (NEFF, 1979; SOCLO *et al.*, 2000), the elevated parent-PAH concentrations on this location are assumed to be a consequence of former industrial activities. Over the past twenty years, the most expressed PAH-generating activity on this location has been traffic, both inland and marine, which also contributes to the high parent-PAH concentration at CS10 station (NEFF, 1979).

At the rest of the studied coastal stations, T-PAH concentrations ranged from 139,54 $\mu\text{g kg}^{-1}$ (CS1) to 1005,29 $\mu\text{g kg}^{-1}$ (CS2), corresponding to moderate state of pollution (ARIAS *et al.*, 2011). Parent-PAH was the dominant fraction at most of these stations, indicating a prevalence of pyrogenic sources such as domestic heating, biomass burning, marine and inland transport. (BDZUSEK *et al.*, 2004; BOONYATUMANOND *et al.*, 2006). The concentration of Me-PAH fraction (428,01 $\mu\text{g kg}^{-1}$) was higher than the concentration of parent PAH (327,40 $\mu\text{g kg}^{-1}$) only at CS2 station, indicating that petrogenic sources, i.e., unburned fossil fuels, are the main source of PAH pollution at this location (NEFF, 1979; STOUT *et al.*, 2004; WANG *et al.*, 2007).

PAH concentrations determined on four locations in the Kaštela Bay are shown in Fig. 3.

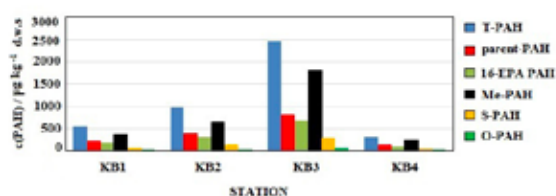


Fig. 3. Concentration of total PAH (T-PAH), 16 EPA priority PAH (16 EPA PAH), unsubstituted PAH (parent-PAH), methyl substituted PAH (Me-PAH), sulphur containing PAH (S-PAH) and oxygen containing PAH (O-PAH) at investigated stations in the Bay of Kaštela

The highest T-PAH concentrations in Kaštela Bay were observed at station KB3, which is located near the industrial port of Split and the shipyard area. This station is located in the confined, eastern part of the bay, which doesn't allow efficient water exchange, resulting in accumulation of pollutants in the sediment.

Level of pollution on this site can be described as highly polluted (ARIAS *et al.*, 2010) with values similar to those reported for the sediments of the urbanised areas of the Ionian Sea (STORELLI & MARCOTRIGIANO, 2000) and the western Mediterranean (LIPIATOU *et al.*, 1991). The concentration of Me-PAH fraction was higher than the concentration of unsubstituted, parent PAH fraction, indicating prevalence of petrogenic sources in the Kaštela Bay, such as accidental spills of oil and other oil-derived products used in ship maintenance.

T-PAH concentrations in sediment from eight stations in the Šibenik Bay (Fig. 4) exceed values of 5000 $\mu\text{g kg}^{-1}$, indicating a very high level of pollution in the entire Bay (ARIAS *et al.*, 2010). The worst situation was observed at station SB8 located near former ferroalloy factory, where T-PAH concentration of 26145,62 $\mu\text{g kg}^{-1}$ was measured. Parent-PAH compounds were the dominant compounds in the sediment of each station in Šibenik Bay which is typical for the combustion derived PAH mixtures (NEFF, 1979). A high proportion of Me-PAH in total concentrations of PAH was measured at SB1, where the concentration of Me-PAH fraction (6299,82 $\mu\text{g kg}^{-1}$) was almost equal to the concentration of parent PAH compounds (6455,55 $\mu\text{g kg}^{-1}$). Station SB1 is located near the tourist marina in the eastern part of the bay, suggesting that high contribution of petrogenic PAH in the sediment of this station is a consequence of vessel maintenance, which mainly occurs outside the tourist season, especially during the winter period when sediments at SB1 station were sampled (MANDIĆ *et al.*, 2018).

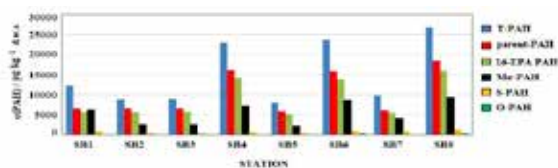


Fig. 4. Concentration of total PAH (T-PAH), 16 EPA priority PAH (16 EPA PAH), unsubstituted PAH (parent-PAH), methyl substituted PAH (Me-PAH), sulphur containing PAH (S-PAH) and oxygen containing PAH (O-PAH) at investigated stations in the Bay of Šibenik

Very high PAH concentrations, observed at each station in Šibenik Bay, are similar to those

observed in the sediments of great Mediterranean ports and industrialised areas worldwide (BAUMARD et al., 1998.) such as Port of Napoli (SPROVIERI et al., 2007), Toulon harbour (BENLACHEN et al., 1997) and Mexico Bay (PONCE-VELEZ et al., 2006.). PAH levels determined in the sediments of Šibenik Bay are also similar to the PAH values reported for the Port of Rijeka, that is situated in the Northern Adriatic and is under high anthropogenic pressures (ALEBIĆ-JURETIĆ, 2011). The entire area of Šibenik bay can be considered as a „HOT SPOT“ area regarding the PAH pollution (ARIAS et al., 2010.). Due to the high persistence of PAH in aquatic environments of high salinity, temperature and high organic content

in the sediment (MARINI et al., 2013), it can be concluded that the high PAH concentrations in the sediments of the entire Šibenik Bay are due to industrial activities in the past, rather than due to the recent inputs from maritime activities.

Application of SQG for environmental risk assessment

Application of sediment quality guidelines, proposed by CCME, in the coastal area revealed excellent sediment quality at eight coastal stations: CS1, CS2, CS4, CS5, CS6, CS7, CS8, CS9 and CS11 (Table 3). Concentrations of all examined compounds on these stations were below threshold effect level (TEL).

Table 3. Environmental risk assessment according to CCME guidelines for Sediment Quality Assessment (TEL= threshold effect range low; PEL= probable effect level) (CCME, 2001)

CCME	N	ACY	ACE	F	PHE	A	FLA	PY	BaA	CHR	BbjFL	BkFL	T-PAH
TEL ($\mu\text{g kg}^{-1}$)	30	10	10	20	90	50	110	150	70	110	70	60	870
PEL ($\mu\text{g kg}^{-1}$)	390	130	90	140	540	240	1490	1400	690	850	710	610	8040
CS2	13	2	1	5	58	11	42	39	21	25	19	30	1005
CS3	13	0	7	14	138	38	239	207	120	127	288	71	2640
CS10	23	8	3	17	100	35	186	160	94	99	203	49	2643
CS12	7	3	1	6	33	11	69	60	36	41	20	68	960
KB2	10	1	2	6	37	8	60	55	26	34	20	8	1083
KB3	17	0	1	20	90	27	128	120	47	70	78	14	2698
SB1	351	70	673	77	359	85	694	594	389	413	983	292	12545
SB2	27	0	49	54	488	159	894	749	489	526	1125	363	8720
SB3	40	2	45	56	662	146	1040	841	460	490	1100	203	8667
SB4	85	8	135	153	1313	307	2376	1959	1142	1242	2800	811	22174
SB5	14	0	30	37	365	87	819	665	420	466	700	596	7583
SB6	123	11	109	128	1120	266	2321	1969	1143	1271	3147	436	22775
SB7	41	2	79	79	540	105	785	690	419	558	563	354	9869
SB8	117	8	177	184	1448	331	2831	2298	1370	1483	2485	1351	26145

The highest environmental risk was observed at stations CS3 and CS10. Concentrations of PHE, FLA, PY, BaA, CHR, BFL and T-PAH at station CS3 were within TEL-PEL range, which corresponds to the occasional occurrence of

adverse biological effects. Similar results were observed at station CS10, where the concentrations of PHE, FLA, PY, BaA, BbjFL and T-PAH were above TEL but below PEL value. At stations CS2 and CS12, only T-PAH concentrations

Table 4. Environmental risk assessment according to NOAA guidelines for sediment quality assessment - SQA (ERL=effect range low; ERM=effect range medium)

NOAA	N	ACY	ACE	F	PHE	A	FLA	PY	BaA	CHR	Bbfl	Bkfl	T-PAH
ERL ($\mu\text{g kg}^{-1}$)	160	40	20	20	240	90	600	660	260	380	320	280	3500
ERM ($\mu\text{g kg}^{-1}$)	2100	640	500	540	1500	1100	5100	2600	1600	2800	1880	1620	23580
SB1	351	70	673	77	359	85	694	594	389	413	983	292	12545
SB2	27	0	49	54	488	159	894	749	489	526	1125	363	8720
SB3	40	2	45	56	662	146	1040	841	460	490	1100	203	8667
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SB8	117	8	177	184	1448	331	2831	2298	1370	1483	2485	1351	26145

were in the TEL-PEL range within which harmful effects are occasionally observed.

In Kaštela Bay, T-PAH concentrations were above TEL value at stations KB2 and KB3, but below PEL value, indicating a moderate risk for environmental health associated with T-PAH concentrations. At KB3 station, concentrations of ACE, F and PHE were also in the TEL-PEL range, confirming that a moderate environmental risk is expected at this station.

In Šibenik Bay, the concentrations at each station were above PEL value for at least one examined PAH compound. The worst situation was observed at station SB8, where concentration of ACY was below TEL; N was above TEL, but below PEL, while the concentrations of all other studied compounds were above PEL value, at which adverse effects frequently occur. A similar situation was found at station SB4, where ACY was below TEL, F and N were below PEL but above TEL, and all other compounds were above PEL value. Both stations are located near the area where ferroalloy factory operated from 1881 to 1990, with station SB8 being closer to the exact location. At SB5 station, concentration of all a moderate environmental risk was determined. The concentrations of N, ACY and ACE at this station were lower than TEL

values, while concentrations of all other compounds were within TEL-PEL range. A similar situation was observed at station SB7, where ACY concentration was below TEL and T-PAH concentration above PEL while the concentrations of other studied compounds were above TEL, but below than PEL values, corresponding with a concentration range within which adverse effects occasionally occur. Total PAH concentrations exceeded PEL values at every station in the Šibenik Bay, except for one station – SB5, which corresponds with a concentration range within which adverse effects frequently occur (LONG *et al.*, 1995; MACDONALD *et al.*, 2000; CCME, 2001).

The results of application of SQG proposed by NOAA are shown in the table 4.

It was shown that concentrations of all PAH compounds in the sediment of twelve coastal station, as well as in the Kaštela bay, were below ERL value, indicating that there's no risk for environmental health associated with PAH pollution on these locations (LONG *et al.* 1995; NOAA *et al.*, 1998; MACDONALD *et al.*, 2000). In Šibenik Bay, concentrations of N and ACY were below ERL, indicating minimal adverse environmental effects. Concentrations of ACE, FL, PHE, ANT, FLA, PY and BaA were higher than ERL but

lower than ERM, corresponding to the concentration range within which adverse effects occasionally occur. Moderate risk was also observed for CHR concentrations at all stations in Šibenik Bay. For the concentrations of BbJFL, a moderate risk was calculated for SB1, SB2, SB3, SB5 and SB7, while for BkFL a moderate risk was observed at stations SB3, SB6 and SB8. At the remaining stations, BkFL concentrations were below ERL value. At stations SB4, SB6, and SB8, BbjFL concentrations were above ERM, indicating a high environmental risk associated with these PAH compounds. According to the T-PAH concentrations, a high environmental risk (>ERM) was observed at station SB8, while at the other stations in Šibenik bay T-PAH concentrations were within a concentration range where adverse effects occasionally occur.

Results of application of SQG that are recommended by OSPAR commission are shown in table 5.

Sediment quality assessment according to OSPAR recommendations revealed moderate

environmental risk for at least one examined compound at 6 coastal stations: CS2, CS3, CS4, CS6, CS10 and CS12, respectively.

At stations CS2, CS3 and CS10, moderate environmental risk was calculated for N, PHE, A, FLA, PY, BaA and CHR, while at stations CS2 and CS10, BaP concentrations also corresponded to moderate environmental risk. At station CS12, concentrations of PHE, A, FLA, PY, BaA, CHR and BaP were above BAC, but below ERL, indicating a moderate environmental risk at this station. Moderate risk was also observed at station CS4 for sediment concentrations of A, FLA, PY, BaA and CHR, which were within BAC-ERL range. At station CS6, only PY concentration was slightly higher than BAC, suggesting that on this station low environmental risk is present. At the other coastal stations, concentration of all studied compounds was below BAC, indicating low environmental risk (OSPAR, 2004). In Kaštela bay, the concentrations of N, PHE, A, FLY, PY, BaA and CHR at stations KB2 and KB3 were above BAC, but below

Table 5. Environmental risk assessment according to the guidelines for sediment quality assessment proposed by OSPAR commission. (BAC=background assessment concentrations; ERL=effect range low)

OSPAR	N	PHE	A	FLA	PY	BaA	CHR	BaP	IP	BPER
BAC ($\mu\text{g kg}^{-1}$)	8	32	5	39	24	16	20	30	103	80
ERL ($\mu\text{g kg}^{-1}$)	160	240	85	600	665	261	384	430	240	85
CS2	13	58	11	42	39	21	25	19	0	10
CS3	13	138	38	239	207	120	127	136	6	1
CS4	5	23	7	49	41	28	23	26	27	21
CS6	2	18	5	34	27	15	20	17	18	15
CS10	23	100	35	186	160	94	99	98	74	64
CS12	7	33	11	69	60	34	41	35	34	27
KB1	4	23	7	37	33	15	14	9	9	1
KB2	10	37	8	60	55	26	34	11	22	3
KB3	17	90	27	128	120	47	70	23	22	2
SB1	351	359	85	694	594	389	413	454	104	177
SB2	27	488	159	894	749	489	526	558	25	208
SB3	40	662	146	1040	841	460	490	517	22	157
SB4	85	1313	307	2376	1959	1142	1242	1406	66	403
SB5	14	365	87	819	665	420	466	494	374	175
SB6	123	1120	266	2321	1969	1143	1271	1395	108	384
SB7	41	540	105	785	690	419	558	462	323	115
SB8	117	1448	331	2831	2298	1370	1483	1577	119	459

ERL value. At station KB1, only ANT and PY were above BAC but below ERL while at KB4 concentrations of all studied compounds were below BAC value. According to these results, a moderate environmental risk can be expected in Kaštela Bay, except in the western part, which is the most distanced from industrialised parts of the bay, where a low environmental risk was observed.

At every station in Šibenik Bay, N concentrations were above BAC value and below ERL, except at the station SB1 where N concentrations were above ERL value. concentrations of all other examined PAH compounds were above ERL value, suggesting frequent occurrence of adverse effects. The highest environmental risk was observed at stations SB5 and SB7 where the concentrations of only one PAH compound were below ERL, while concentrations of other compounds were in the range within which adverse effects frequently occur (>ERL).

High environmental risk was observed for the entire Šibenik Bay with concentrations of eight examined compounds exceeding ERL at six stations: SB1, SB2, SB3, SB4, SB6 and SB8. The worst situation in Šibenik Bay, according to OSPAR recommendations, have been observed at SB5 and SB7 station, where concentrations of N were within BAC-ERL range, while concentration of other studied compounds were above ERL value.

Regardless of which SQG was applied, the highest risk was identified in the Šibenik Bay, indicating poor environmental quality and frequent occurrence of adverse biological effects. Moderate environmental risk according to the CCME and OSPAR recommendations was observed for stations KB2 and KB3 in Kaštela Bay and for 4 coastal stations: CS2, CS3, CS10 and CS12. In Kaštela Bay, the highest environmental risk was recorded at station KB3 for two sets of SQG, CCME and OSPAR recommendations, respectively.

Assessment of acute sediment toxicity

The results of acute toxicity of sediment extracts are presented in Table 6. The results are expressed as the reciprocal value of LD50, which describes the concentration of sediment extract that causes a 50% decrease in bacterial bioluminescence (BIHARI *et al.*, 1989; BIHARI *et al.*, 2006; FERNANDEZ-PINAS *et al.*, 2014).

The results showed high acute sediment toxicity at station CS3 in the coastal region associated with very poor sediment quality. Poor sediment quality was measured at stations CS9 and CS11 station, while excellent sediment quality with very low acute toxicity was observed at the remaining stations in the coastal area. In Kaštela Bay, high acute toxicity, corresponding to very

Table 6. Toxicity of sediments and sediment toxic status at investigated stations. LD50 is a lethal dose of sediment extract at which bacteria bioluminescence decrease for 50%

Station	Toxicity (1/LD50*1000)	Toxic Status	Station	Toxicity (1/LD50*1000)	Toxic Status
CS1	5	EXCELLENT	KB1	50	POOR
CS2	5	EXCELLENT	KB2	5	EXCELLENT
CS3	166	VERY POOR	KB3	200	VERY POOR
CS4	5	EXCELLENT	KB4	5	EXCELLENT
CS5	5	EXCELLENT	SB1	100	POOR
CS6	5	EXCELLENT	SB2	19	GOOD
CS7	5	EXCELLENT	SB3	15	GOOD
CS8	5	EXCELLENT	SB4	150	VERY POOR
CS9	34	POOR	SB5	298	VERY POOR
CS10	5	EXCELLENT	SB6	500	VERY POOR
CS11	28	POOR	SB7	500	VERY POOR
CS12	20	GOOD	SB8	500	VERY POOR

poor environmental status, was determined at station KB3, located in the eastern part of the bay, where pollution from anthropogenic activities is the most expressed. Poor environmental status in Kaštela Bay was also detected on KB1, while excellent environmental status was observed at the other stations. In Šibenik Bay, very poor environmental status was determined at six out of eight stations, indicating high acute toxicity of the sediment and thus very poor environmental quality.

Comparing the sediment toxicity results with the SQA results, it is observed that NOAA predictions greatly underestimated the environmental risk, especially in the coastal zone and Kaštela Bay. At two stations in Šibenik bay, sediment status was described as good, which contradicts observations based only on sediment PAH concentrations. Good sediment status on these stations is probably due to the greater distance of these two stations from the main source of pollution in the Šibenik Bay (MANDIĆ *et al.*, 2018). The SQA results according to CCME and OSPAR are in better agreement with bioassay results, but still greatly differ. This discrepancy between the results is likely due to the presence of other toxic compounds in the sediments that were not encompassed with this study, such as heavy metals, pesticides, dioxins and other xenobiotics, which also cause a decrease in bacterial bioluminescence (BIHARI *et al.*, 2006; FERNANDEZ-PINAS *et al.*, 2014). In addition, the Microtox bioassay measures acute toxicity only for one bacterial specie, whereas SQG were developed to predict risk to various marine organisms as well as for the human health and takes into account carcinogenic and potentially carcinogenic PAH compounds, which may also explain differences between the results (LONG *et al.*, 1995; MACDONALD *et al.*; 2000).

Acute sediment toxicity results were compared with concentrations of specific PAH groups to determine which PAH fraction had the strongest relationship with results of acute toxicity measurements. Linear regression correlation coefficients (R^2) between sediment acute toxicity and concentrations of specific groups of PAH compounds were calculated and given in the

table 7. The strongest correlation was obtained for the S-PAH fraction with an R^2 coefficient of 0,69.

Table 7. Coefficients of linear correlation between concentration of specific PAH groups and sediment toxicity in the studied area

PAH group	R^2
T-PAH	0,5601
16 EPA-PAH	0,5358
parent- PAH	0,514
Me-PAH	0,5497
S-PAH	0,6866
O-PAH	0,5394

The correlation coefficients for the other groups of PAH ranged from 0,5 to 0,57, which can be considered as moderately strong relationship. Sulphur-containing compounds such as DBT, are readily biodegraded to benzotriophene diols (NEFF, 1979; BRESSLER & FEDORAK, 2001). These degradation products are more toxic and more bioavailable due to their greater polarity, which may partially explain the strong correlation coefficient between acute sediment toxicity and concentrations of S-PAH. However, the acute sediment toxicity results should be cautiously interpreted since toxicity of sediment extracts may be caused by toxic compounds other than PAH, e.g., heavy metals, pesticides, dioxins, and other xenobiotics (BIHARI *et al.*, 2006; FERNANDEZ-PINAS *et al.*, 2014).

CONCLUSIONS

Application of SQGs revealed high environmental risk for the entire Šibenik Bay area. Moderate environmental risk was observed for station KB3 in Kaštela Bay and for four coastal stations: CS2, CS3, CS10 and CS12. At the remaining studied stations, a low environmental risk was calculated according to the sediment PAH concentration. The very low acute toxicity, corresponding to excellent sediment quality at the sites where SQG application indicated high environmental risk suggests caution when evaluating environmental quality based only on PAH

concentration, since the reason for increased toxicity may originate from toxic compounds other than PAH. Moreover, SQGs applied in this study were developed mainly to evaluate potential chronic toxicity as they take into consideration mostly persistent, high molecular weight PAHs, which are enlisted as carcinogenic or potentially carcinogenic. Microtox assay, on the contrary, provides results based on measurements of acute toxicity of sediment extracts, which is primarily caused by the presence of low molecular weight PAH and their alkylated counterparts. This PAH fraction is more soluble and bioavailable than the high molecular, parent PAH compounds and thus more likely to cause acute toxicity. Another limitation of the bioassay application is that acute toxicity is only tested for the bacteria, suggesting that higher organisms, especially vertebrates, react differently when exposed to contaminated sediments. Therefore, to obtain more accurate results acute sediment toxicity, bioassays with more complex organisms may be needed. It can also be concluded that the SQGs proposed by CCME and the OSPAR commission provide more accurate assessment of environmental risk, while NOAA's set of SQG

underestimate the risk associated with PAH and shouldn't be used for SQA in the Adriatic Sea.

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Određivanje toksičnosti sedimenta povezane s policikličkim aromatskim ugljikovodicima – PAH duž istočne obale Jadranskog mora

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SAŽETAK

Policiklički aromatski ugljikovodici - PAH istraživani su u sedimentu na 24 lokacije u priobalnom području Jadranskog mora. Ukupna koncentracija PAH-ova u sedimentu (T-PAH) iznosila je od 14,98 do 26415 $\mu\text{g kg}^{-1}$. Najviša vrijednost masenog udjela T-PAH –ova izmjerena je u sedimentu Šibenskog zaljeva. Na većini postaja u Priobalnom području te na svim postajama u Šibenskom zaljevu, ne-supstituirani PAH-ovi bili su dominantni spojevi u sedimentu; dok je sediment na svim postajama u Kaštelanskom zaljevu bio obogaćen metil-supstituiranim PAH-ovima (Me-PAH). Kako bi se odredila toksičnost sedimenta te procijenila opasnost za zdravlje okoliša, kvaliteta sedimenta istražena je primjenom triju različitih smjernica za procjenu stanja sedimenta - SQG. Visok rizik za okoliš izračunat je za sve lokacije u Šibenskom zaljevu; za jednu postaju u Kaštelanskom zaljevu, smještenu u blizini industrijske luke Split; te za dvije postaje u priobalju. Nizak rizik za zdravlje okoliša utvrđen je na postajama udaljenim od urbanih područja kao što je otok Pag. Akutna toksičnost sedimenta dodatno je analizirana mjerenjem smanjenja intenziteta bakterijske bioluminiscencije nakon izlaganja ekstraktima uzoraka sedimenta.

Dobiveni rezultati o akutnoj toksičnosti razlikuju se od rezultata dobivenih primjenom smjernica za procjenu kvalitete sedimenta. Ekstrakti uzoraka sedimenta u kojima su izmjerene niske vrijednosti masenih udjela PAH-ova uzrokovali su visoku akutnu toksičnost iz čega proizlazi da procjena toksičnosti sedimenta uzimanjem u obzir samo masenih udjela PAH-ova u sedimentu nije dobar pokazatelj stanja toksičnosti sedimenta. Analizom korelacije između masenih udjela specifičnih grupa PAH-ova u sedimentu i akutne toksičnosti ekstrakata sedimenta, utvrđena je jaka povezanost toksičnosti sa skupinom PAH-ova koji u svojoj strukturi sadrže atom sumpora (S-PAH), što upućuje da je prilikom procjene stanja sedimenta potrebno uzeti u obzir i S-PAH-ove.

Ključne riječi: PAH; sediment; Jadransko more; procjena kvalitete sedimenta; biološki test; onečišćenje mora