Polycyclic aromatic hydrocarbons in surface sediments of the mid-Adriatic and along the Croatian coast: Levels, distributions and sources

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Abstract :

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

Graphical abstract
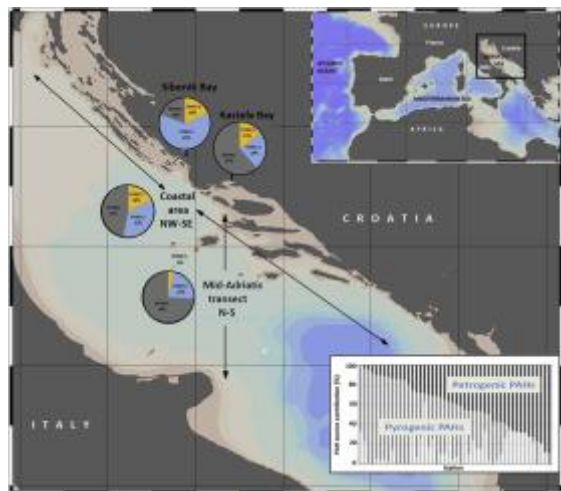
Highlights

► The high levels of sedimentary PAHs are related to discharge/emission sites. ► The strong gradients of PAH levels are found at local and regional scales. ► The parent and alkyl homologues appear as first-hand indicators of PAH sources. ► Petrogenic PAHs are spatially more widespread in the mid Adriatic. ► Pyrogenic PAHs are more closely related to the point discharge sources.

Keywords : Marine sediments, Polycyclic aromatic hydrocarbons (PAHs), Source profiles Source apportionment, Source-receptor models

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widespread organic pollutants in current marine and terrestrial environments (Laflamme and Hites 1978). Although certain of these hydrocarbons also have natural origins, anthropogenic PAHs predominate in today's environments (Neff 1979, Venkatesan 1988, Wakeham et al. 1980). A large number of anthropogenic PAHs are recognized as strong mutagens and carcinogens (Allen et al. 1998, Durant et al. 1998), representing a significant public health concern and threats to ecosystems. Actually, PAHs are on the lists of priority pollutants and substances in the USA and Europe, aiming at better control, regulation and the reduction of water and air pollution by these chemicals (EPA 2014, EU 2013). The effective mitigation and remediation measures of this pollution require an understanding of the various sources of PAH contributions found in a specific region. In the marine environment, the major sources of anthropogenic PAHs are related to releases of crude petroleum and its numerous derivatives and to all inputs of compounds derived from the incomplete combustion of biomass and fossil- and modern bio-fuels (Fraser et al. 1998, Dachs et al. 2002, Deyme et al. 2011). The pathways of petroleum-derived PAHs are mainly regular spillages from various maritime activities (transport, oil exploitation, harbour operations…) as well as accidental oil spills, whereas combustion-derived PAHs (generally from marine and continental transport, power and heat plants, residential warming and specific industries) enter the marine environment mainly via the atmospheric fallout of soot particles and

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62 continental watershed runoff, including, direct discharges of storm waters from coastal large

63 coastal cities and industrialized sites (Lima et al. 2005, Guo et al. 2007, Gonul and Kucuksezgin

64 2012). Due to strong sorption propensity, many environmental PAHs are associated with particles

65 (Karickhoff et al. 1979, Dachs et al. 2002, Zhao et al. 2013). Despite their long-range global

66 atmospheric transport (Fernandez et al. 2000, EEA 2013), PAHs are also deposited in large

67 amounts in coastal sediments, showing a strong decline of their concentrations with increasing

68 distance from the coast (Lipiatou et al. 1997, Tsapakis et al. 2003, Cathalot et al. 2013).

69 In this context, complementary and alternative approaches for the characterization of PAH

70 sources are continuously developed. Common emissions and discharge inventory studies have

71 provided emerging regional and local trends, and a generally good correspondence between

72 emissions of PAHs and records of energy production and fossil-fuels consumption (Zhang et al.

73 2009, EEA 2013, Shen et al. 2013). However, highly variable emission factors have been

74 reported, thus indicating great uncertainties in the environmental inventories of PAHs (Jenkins et

75 al. 1996, Pacyna et al. 2003, Johansson et al. 2004, Lee et al. 2005, Chen et al. 2005). Many

76 reported studies are based on the understanding of spatial distributions and the identification of

77 point emission sources, the interpretations of compositional molecular signature fingerprints and

78 diagnostic source ratios of specific PAHs determined in diverse receptor compartments, namely,

79 the atmosphere, sediments, biota (Douglas et al. 1996, Yunker et al. 2002, Neff 2002,

80 Christensen et al. 2004, Zhang et al. 2005). More recently, chemometric analyses have also been

81 applied for PAH source characterization (Larsen and Baker 2003, Li et al. 2003, Comero et al

82 2009, Stout and Graan 2010). This approach is often referred to as the source apportionment

83 method, allowing the determination of a number of contributing sources as chemical profiles

84 ("end-member" signature fingerprints) and the relative amounts of each source present in a

85 sample. For instance, in the urban atmosphere of Baltimore, based on multivariate statistics and

86 receptor environment models, such methods allowed the resolution and apportionment of up to

87 six combustion sources of PAH (Larsen and Baker 2003). Finally, the radiocarbon analysis of

88 individual PAH compounds in different sedimentary and atmospheric environments was also

89 used as the most reliable method to determine the relative contributions of fossil fuel and biomass

90 combustion sources of PAHs (Mcare et al. 2000, Reddy et al. 2002, Mandalakis et al. 2004,

91 White et al. 2005, Mandalakis et al. 2005, Kumata et al. 2006, Cathalot et al. 2013). Such

92 determinations, using PAHs as excellent molecular tracers of combustion particles, may also

93 contribute to more fundamental assessments of pyrogenic/combustion carbon contributions to

94 various pools of organic carbon budgets, and therefore are carried out as well in the context of

95 global climate change studies (White et al. 2005, Dickens et al. 2004). However, this later

96 method is very demanding and reserved for specialized laboratories.

97 In this study, we report on PAH levels, distributions and source characterization determined in

98 the surface sediment of the mid-Adriatic and along the Croatian coast. Extensive analyses of

99 PAHs in the sediment samples included unsubstituted parent compounds, alkyl-substituted

100 homologues and sulphur heterocyclic compounds. Four zones were studied: the mid-Adriatic

101 transect, a coastal survey from the north-west to the south-east along the Croatian shoreline and

102 two urban-industrial zones: Šibenik and Kaštela bays. This regional/local geographical coverage

103 was arranged so that it included known and suspected contaminant emission sites and reference

104 sites away from direct pollution sources. Finally, PAH source characterization in this study is

105 based on the wide range of analyzed compounds, together with geographical distribution data it

106 also includes an examination of carefully selected meaningful source-specific diagnostic ratios

107 and correlations, explanatory multivariate statistics by principal component (PCA) and

108 hierarchical cluster (HCA) analyses, and chemometrics receptor environment analysis using the

109 alternative least square (ALS) calculation method. The results include the identification of PAH

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110   chemical source profiles and the quantification of the relative contributions of these sources in

111   the studied areas. Consequently the results presented provide a coherent set of reference data on

112   the contamination of marine sediment by PAHs in the mid-Adriatic and along the Croatian coast.

113   **2. Materials and methods**

114   **2.1. Sample collection and pre-treatment**

115   Sediment samples were collected from the *R/V Bios* 2 (IOF/Croatia) during three campaigns in

116   2013. In total, 29 stations were sampled in the four studied areas: the mid-Adriatic transect, a

117   coastal survey from north-west to south-east along the Croatian shoreline (from 44.49005 N and

118   15.01010 E to 42.63339 N and 18.02187 E) and two urban-industrial sites, Šibenik and Kaštela

119   bays (Fig. 1, Table S-1 and S-2). Approximately, 200 grams of wet surface sediment were

120   manually sub-sampled using stainless steel spatula from the centre of Van Veen Grab. The grab

121   sampling may roughly represent 0.1 m^2 of surface sediment. The sediment sub-samples were

122   wrapped in pre-cleaned aluminium foil and subsequently frozen on-board at -20°C. Samples were

123   transferred frozen to the laboratory, freeze-dried and subsampled for the chemical and sediment

124   characterization analysis. The sediment aliquots for PAH analyses, were further sieved through a

125   2 mm stainless steel screen and stored in pre-cleaned glass jars until laboratory analyses.

126   **2.2. Grain size distribution**

127   A weighted sample aliquot of dry granular sediment is processed through a nested set of

128   standardized sieves with progressively smaller openings of: 4, 2, 1, 0,5, 0,25, 0,125 and 0,063

129   mm. The smaller than 0.063 mm sediment fraction was determined by the aerometric method

130   according to Casagrande (Ostrowska et al, 1991). The fractions were described according to

131   Wentworth Grade Scale (1922): gravel-sized particles have a nominal diameter of 2 mm; sand-

132   sized particles have nominal diameters of <2 mm to >63 µm; silt-sized particles have nominal

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133   diameters of <62.5 µm to >4 µm; and clay is < 4 µm. The parameters calculated for grain size

134   include: mean, median, sorting and skewness (Table S-2).

135   **2.3. Organic matter determination**

136   The amount of organic matter was determined by gravimetric measurements as lost by ignition

137   at 450 °C. Approximately 0.5 g of a dried, ground and sieved (4 mm) sediment sample aliquot is

138   weighted precisely in a crucible. Crucibles are then dried at 110 °C for 24 hours. When cooled,

139   the crucibles are reweighed and treated with 30% H_2O_2. Once the samples have been dried, the

140   crucibles are placed in a furnace and ignited at 450 °C for six hours.

141   **2.4. PAH analysis**

142   The analytical method is described in more detail elsewhere (Tronczyński et al. 2004).

143   Briefly, the analysis of PAHs in the surface sediment included different groups of unsubstituted

144   parent compounds (PAH), alkyl-substituted homologues (C-PAH) and both unsubstituted and

145   alkyl-substituted polycyclic aromatic sulphur heterocyclic compounds (SPAH and C-SPAH). The

146   concentrations were determined for individual compounds and for their alkyl-substituted

147   homologue groups (Table S-3). Aliquots of dry sediments (5 – 20 g) of each sample were

148   extracted twice using dichloromethane by accelerated solvent extraction (Dionex ASE 200). Prior

149   to extraction, sediment samples were spiked with perdeuterated recovery standards

150   (phenanthrene-d_{10}, benzo[*e*]pyrene-d_{12} fully deuterium labelled compounds).   The organic

151   extracts were concentrated using rotary evaporation and nitrogen gas and then purified and

152   fractionated by a two-layer 5% deactivated silica/alumina column. The PAHs were analysed and

153   quantified by gas chromatography coupled to the mass selective detectors (GC-MS Agilent

154   Technologies models 7890/5975). Prior to GC-MS analysis, all sample extracts and calibration

155   solutions in auto-sampler vials were quantitatively spiked using a robotic auto-sampler with an

156   internal standard mixture containing deuterated compounds: acenaphtene-d_{10}, fluorene-d_{10},

157 pyrene-d_{10}, benz[a]antracene-d_{12} and indeno[1,2,3-cd]pyrene-d_{12}. The quantification of individual

158 PAH compounds and group of their alkyl-homologues in the samples was carried out by using

159 corrected response of GC-MS with the response of correspondent surrogate quantification

160 standard. The replicate analysis of EC-2 NWRI (Environment Canada) sediment samples of

161 certified reference material for PAHs was used for the assessment of the precision and accuracy

162 of the entire analytical protocol.   The accuracy was between 60 and 93 % of certified values (n =

163 6) and relative standard deviation of repeated analysis was better than ± 16% for all quantified

164 PAH analytes in the sediment samples. Average recovery of standards (phenanthrene-d_{10} and

165 benzo[e]pyrene-d_{12}) was 73 ± 16% while samples with low recovery (<50%) were excluded.

166 **2.5. Statistics**

167 Hierarchical cluster (HCA) and principal component analysis (PCA) of PAH data were

168 performed using Pirouette multivariate data analysis software (Infometrix 2014). For both

169 analyses the PAH concentration data were pre-processed by autoscaling, i.e. mean-centering

170 followed by variance scaling. For HCA we used Euclidean distance between samples, expressed

171 on the standard scale of similarity where a value of 1 is assigned to identical samples and a value

172 of 0 to the most dissimilar samples. The samples were clustered by the incremental link method

173 used to calculate inter-cluster distances (i.e. a sum of squares approach). For PCA, total

174 variability of the original PAH data is represented by a minimum number of factors with a

175 subsequent varimax (normal) rotation of factors, which maximizes the variance of the loadings

176 by sequentially rotating PCA loadings pair-wise. Finally, in the receptor model, the problem is

177 considered as a solution of the chemical mass balance equation in a number of source profiles,

178 and their contributions to each individual sample. The number of sources is related to total

179 variance, where the alternating least square (ALS) calculation requires an iterative technique to

180 obtain the most meaningful solution, that is, the best fitting compositions and profiles (Tauler et

181 al. 1993). The algorithm used in the present estimates, is based on "convexity" calculation

182 (Grande and Manne 2000), it finds the purest "shapes" in the original PAH concentration data,

183 determining row-wise estimates of profiles, and column-wise estimates of composition

184 (Pirouette, Infometrix 2014). The source profiles are interpreted as source types

185 (combustion/pyrogenic and petroleum/petrogenic), also using known emission/discharge

186 information and geographical distribution results.

187 **3. Results and discussion**

188 **3.1. Levels, spatial distributions and gradients**

189 Concentrations of main suites of PAH determined in the sediments of four studied areas (mid-

190 Adriatic transect, coastal transect, Kaštela and Šibenik bays) are summarized in Table 1 and

191 further detailed in SI (Fig. S-1 and Table S-4). The summed concentrations of parent and alkyl-

192 PAH ranged from 8.50 to 18348 µg kg^{-1} and from 2.95 to 5770 µg kg^{-1} dry weights, respectively.

193 Levels of parent and alkylated sulphur heterocyclic PAHs (ΣS-PAH, ΣCS-PAH) were within the

194 ranges 0.336 – 514 µg kg^{-1} and 0.292 – 977 µg kg^{-1} d.w., respectively.

195 The lowest concentrations of summed total PAHs (ΣT-PAH), were determined along the mid-

196 Adriatic transect (ΣT-PAH, range 11.7 – 282 µg kg^{-1}, d.w.), the intermediate levels were

197 determined in the coastal and Kaštela bay sediments (ΣT-PAH, range 117 – 2580 µg kg^{-1}, d.w.)

198 and the highest level of contamination by PAHs was found in Šibenik bay (ΣT-PAH, range 6610

199 – 24576 µg kg^{-1}, d.w.). The very low concentrations determined along the transect (especially at

200 off-shore stations TS1 and TS2) correspond to PAH levels reported in sediments from open sea

201 areas in the eastern Mediterranean and Cretan Sea (Lipiatou et al. 1997, Tsapakis et al. 2003,

202 Gogou et al., 2000, Gonul and Kucuksezgin 2012) and also from remote locations of the world

203 oceans, such as the Barents Sea (Savinov et al. 2003) and arctic lakes (Fernandez et al. 2000).

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204   These levels remain within the range of background reference concentrations of PAH in marine

205   sediments (Ospar/Ices 2004, Azoury et al. 2013, UNEP 2016). Interestingly, higher

206   concentrations along the mid-Adriatic transect were found at stations TS3 and TS5. The

207   concentrations increase systematically from TS1 to TS3 probably indicating a local concentration

208   gradient in this area. TS3 is located along the route of the densest maritime traffic in the Adriatic

209   (Morovic et al. 2015). Furthermore, a higher amount of silt and clay in the sediment at this station

210   may also contribute to the effective deposition of PAHs (Table S-2). Relatively high levels of

211   both parent and alkylated PAH homologues were also found at station TS5, which is

212   approximately 20 miles from the Italian coast. This area is affected by the backward cyclonic

213   gear that spreads contaminants introduced in the Adriatic by the Po valley watershed (Marini et

214   al. 2015). Summed parent-PAH concentrations in the majority of coastal sediments, including

215   Kaštela bay, were within the range that corresponds to the low medium contamination level,

216   which is between slightly below 100 and slightly above 400 µg kg^{-1}, d.w.(Tolosa et al. 1996,

217   Lipiatou et al. 1997, Baumard et al. 1999, Gomez-Gutierrez et al. 2007, Barakat et al. 2011,

218   Mzoughi and Chouba 2011). Relatively high concentrations (> 1000 were µg kg^{-1}, d.w.) were

219   found only at stations CS3 and CS10 in the coastal zone and at station KB3 in Kaštela Bay. At

220   these stations, PAH levels were 2 to 6 times higher than at adjacent sites, indicating local hot

221   spots identified near the town of Zadar (CS3), the site of a former chromium and carbide plant

222   (CS10), and at the shipyard - industrial harbour of Split in Kaštela Bay (KB3). These

223   concentrations are comparable to PAH levels reported for urbanised coastal areas (Benlahcen et

224   al. 1997, Bertolotto et al. 2003, Di Leonardo et al. 2009). In Kaštela Bay, the local gradient is

225   observed for all sampling periods, with concentrations decreasing with increasing distance from

226   the eastern part, near an industrial port (station KB3), to the central part of the bay (station KB4).

227   Furthermore, in the coastal area and Kaštela Bay, for most stations, PAH concentrations in

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228   sediments were within the range corresponding to the average pollution level generally found in

229   areas under moderate anthropogenic pressures, for instance in the Black Sea (Wakeham et al

230   1996), the eastern Mediterranean (Tsapakis et. al 2003), Porto-Tores harbour in Sardinia (De

231   Luca et al. 2004) and Daya Bay in China (Zhou and Maskaoui 2003). Finally, very low coastal

232   concentrations of parent-PAH (< 150 µg kg^{-1}) were determined only at two stations (CS1 and

233   CS7) characterized by high sand content. Such levels correspond to those reported for more

234   remote sea areas, with low pressures from urban and industrial activities, such as the Balearic

235   Islands (127 µg kg^{-1} ,d.w.) and Corsica (87 µg kg^{-1}, d.w.) (Baumard et al.1998, Benlachen et al.

236   1997).

237   High and extremely high concentrations were determined in the Šibenik Bay sediments. The

238   lowest levels found were above 4000 µg kg^{-1},d.w. of parent-PAH, and these values compare to

239   contamination levels in highly industrialised coastal areas in the Mediterranean and worldwide,

240   such as Toulon Harbour (Benlachen et al. 1997), Barcelona Harbour (Baumard et al. 1998),

241   Napoli Harbour (Sprovieri et al. 2007) and the Bay of Mexico (Ponce-Velez et al. 2006). The

242   highest concentrations in the bay were found in the vicinity of the former ferroalloy factory

243   (stations SB4 and SB8), indicating that this historical industrial activity was the main emission

244   source of PAHs in Šibenik Bay. Very significant levels were also found in the harbour area and

245   near-shore in the western part of the Šibenik urban centre (stations SB6 and SB3). The spatial

246   distribution of PAH in the sediments suggests that contamination has spread over the entire bay.

247   However, this contamination seems to remain in Šibenik Bay, given that the PAH concentrations

248   at the closest station outside the bay (CS6), only 2.5 miles away from the entrance to the bay, are

249   10 to 20 times lower (alkyl and parent-PAHs respectively) than the lowest levels determined in

250   the centre of the bay (station SB5). Indeed, limited circulation, water mass exchanges and the

251   local hydrosedimentological regime indicate very poor sediment export to adjacent areas outside

252   Šibenik Bay (Bužančić et al. 2016, Kušpilić 2005).

253   Thus, it appears that the range of PAH concentrations in coastal and mid-Adriatic sediments

254   spans over more than 2000 times between the lowest and the highest contamination levels. In this

255   area, the spatial distributions thus reflect the presence of the strong gradients at local and regional

256   scale, in the contamination of sediments by PAHs. The major factor influencing sedimentary

257   PAH distributions at local scale appears to be the distance from their known continental and

258   coastal upstream emission sites (urban, industrial, harbour…). At a regional scale, however, this

259   distribution depends more on the routes of maritime entry of PAHs (riverine, atmospheric,

260   naval…) and their downstream dispersion, deposition dynamics and sediment type.

261   **3.2. Characterization of PAH sources**

262   The characterization of PAH sources in the environmental samples is generally based on the

263   examination of their chemical composition, allowing the qualitative identification of source

264   signatures (Stogiannidis and Laane 2015) and also, ultimately, the quantitative apportionment of

265   the amount of contaminants contributed by each source (Larsen and Baker 2003, Lang et al.

266   2013). Such characterization might also be supported by the examination of the geographic

267   distribution of PAH concentrations, which would eventually allow assignment of their emission

268   point sources in the studied area. Both of these approaches are selectively used in this study.

269   **3.2.1. Geographic distributions**

270   Based only on the geographic distribution of the sedimentary PAH concentrations in the coastal

271   Adriatic, it was possible to reveal a few point emission sources of PAHs in the studied area. As

272   already discussed above, in the coastal areas characterized by different levels of contamination

273   (i.e. Šibenik Bay and the whole coastal survey including Kaštela Bay), PAH concentrations in the

274   sediments are higher in the areas near emission sources, which may be present or past (Fig. S-1).

275   Thus, in Šibenik Bay, very high levels were found at the stations clearly related to the local point

276   source of PAHs emitted from the former ferroalloy industrial plant (stations SB4 and SB8) and

277   also from mixed sources of PAH releases from urban and harbour /marina facilities (stations

278   SB3, SB1 and SB6). Whereas, along the Croatian coast high concentrations were found near the

279   Zadar urban centre (station CS3), a former metal (iron /chromium) plant (station CS9) and the

280   industrial harbour of Split in Kaštela Bay (station KB3). All these sites should thus be

281   considered as the "hot spots" of sediment contamination by PAHs along the Croatian coast.

282   **3.2.2. Source indicators and classification model-building**

283   The relative PAH abundances, molecular indices and multivariate analysis allow identification

284   and classification of PAH source profiles and contributions (Stogiannidis and Laane 2015). The

285   ratio of alkyl to parent compounds (ΣAlkyl/ΣPAH) was used to assess pyrogenic or petrogenic

286   sources of PAHs in sediments (Yunker et al. 2002). This ratio is sensitive to fresh petroleum

287   releases and was used to distinguish pre- and post-spill contamination after major oil spill events

288   (Short and Harris 1996, Law et al 1999, Tronczyński et al 2004). The threshold values depend on

289   which parent and alkylated homologues are used for calculation of the sum of their totals but, in

290   general a lower than 0.5 ratios are related to pyrogenic sources, whereas a ratio above 1 is more

291   often related to a petrogenic source. In the data presented here, the ΣAlkyl/ΣPAH ratio varies

292   between 0.23 and 1.17 (Table S-5). The lowest values were found in Šibenik Bay indicating the

293   strong contribution of pyrogenic PAHs, whereas the highest ratios were determined at four

294   stations: Kaštela Bay in the industrial northern port of Split (KB3), at transect stations TS4 and

295   TS6 (the first representing the route with highest shipping traffic density in the Adriatic and the

296   second is the closest to the Italian coast, as discussed above, and is influenced by the Po River

297   loads) and at station CS2, i.e.one of the northernmost inner coastal sampling sites with relatively

298   high PAH levels. The application of the ΣAlkyl-PAH/ΣPAH ratio also depends on the correlation

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299 of two variables (Tronczyński et al. 2004). The correlation of parent PAHs with their alkyl

300 homologues thus allows to clearly distinguish the contamination by PAHs in Šibenik Bay from

301 other areas (Fig. S-2).

302 Discrete regression for the Šibenik site, definitely implies specific predominant sources in the

303 bay and that PAH composition is different in the areas outside the bay, with a clearly higher

304 relative contribution of alkyl homologues, indicating greater relative petrogenic inputs. This also

305 suggests that parent against alkyl homologue correlations and ratios might be reliable PAH

306 source indicators for both local and larger geographic areas, and that despite very high

307 concentrations, PAHs from Šibenik indeed remain confined to the bay. Moreover, such indicators

308 of PAH sources in sediments should be less sensitive to degradation/weathering processes,

309 because of the use of summed concentrations of almost all PAHs and their determined

310 homologues. In Šibenik Bay sediments, the indicators clearly withstand past contamination

311 signatures from the ferroalloy plant. These correlations also show (Fig. S-2) that in Šibenik Bay

312 the possible higher contribution of petrogenic PAH, with a relative higher proportion of alkyl

313 homologues, may be inferred at the stations corresponding respectively to Šibenik marina (SB1),

314 the entrance to the Šibenik port (SB 2 and SB7) and one of the samples from the Šibenik fisheries

315 port (SB3) (Fig. S-2). Finally, added points of modelled source profiles of PAH from ALS

316 statistics (see below) align well with the Šibenik regression line for two combustion profiles, as

317 well as for all other stations with the regression line for a petrogenic source.

318 Analogous grouping among samples is obtained by principal component (PCA) and

319 hierarchical cluster (HCA) analyses taking into account the relationships between the

320 independent variables of all determined individual PAH compounds (Fig. S-3). The greatest

321 distance was obtained between the Šibenik Bay stations and all other stations. However, higher

322 variation and dissimilarities may be observed in Šibenik Bay, suggesting an overlap and

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323   combination of distinct PAH sources. Discrete clustering is found for the coastal survey among

324   stations KB3, CS2, CS3 and CS9 that are characterized by higher contamination, in the vicinity

325   of known emissions sources. These findings indicate overall that: geographical distribution, PAH

326   source indices and explanatory multivariate statistics allow coherent categorization of sampling

327   stations, according to the relative contributions of mainly petroleum versus combustion-derived

328   PAHs in the sediments of the studied area. Distinctive characteristics of these sources and their

329   quantitative proportion estimates in each area were further examined by the receptor environment

330   model based on chemometric multivariate statistical analysis.

331   **3.2.3. Source profiles and contributions**

332   Chemometric analysis involving receptor environment models allows the identification of

333   source profiles (PAH fingerprints) and quantitative apportionment of such PAH sources. The

334   algorithm used in the present estimations, is based on multivariate alternating least square (ALS)

335   calculation using the iterative technique (Pirouette, Infometrix 2014). PAH model source profiles,

336   2 combustion profiles and 1 petroleum profile, were obtained by alternative least square analysis

337   (Fig. 2).

338   Both combustion profiles are characterized by higher abundances of unsubstituted PAHs and

339   by "skewed" patterns of parent/alkyl-substituted compounds (phenanthrenes/anthracenes,

340   fluranthenes/pyrenes and chrysenes). In these profiles, greater alkylation homologues were less

341   abundant (C1>C2>C3). The reduced alkylation is consistent with the loss of alkyl side chains

342   during the combustion processes (Lima et al. 2005). Furthermore, different proportions of

343   fluoranthene, pyrene, phenanthrene and benzo[$b+j$]fluoranthenes in two pyrogenic sources,

344   probably discriminate also between different temperature combustion processes, such as motor

345   vehicle engines and open burning (Tobiszewski and Namiesnik 2012). In the range of higher

346   molecular weight, the HMW-PAHs benzo[e]pyrene/benzo[a]pyrene (BePy/BaPy) ratio is lower

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347 than 1 for both pyrogenic profiles (Fig. 2), suggesting non-atmospheric routes of entry and/or that

348 these compounds are not transported far from their emission source (Tobiszewski and Namiesnik

349 2012).

350   In the petrogenic source profile, alkyl-substituted compounds were dominant, with

351 characteristic "bell-shaped" patterns for phenanthrene/anthracene, fluoranthene/pyrene and

352 chrysene suites of compounds. In this petrogenic profile, relatively abundant sulphur heterocycle

353 homologues, such as alkyl-dibenzothiophenes, displaying a bell-shaped distribution may also be

354 noted. However, the significant presence of non-substituted benzonaphthothiophenes (mainly

355 benzo[*b*]naphtho[2,1-*d*]thiophene) may also indicate mixed sources of petrogenic and diesel-

356 combustion emissions (Larsen and Baker 2003). Furthermore, fairly elevated proportions of

357 higher molecular PAHs (benzopyrenes, indeno[1,2,3-*cd*]pyrene (IPy) and benzo[*ghi*]perylene

358 (BghiPy) may also imply a mixed source of PAH for this profile. For this reason, caution should

359 be exercised when interpreting the quantitative results of PAH apportionment by multivariate

360 receptor environment models (Laresen and Baker 2005).

361   The quantitative apportionment of PAH source contributions reveals significant geographical

362 differences (Fig. 3). Dominant petrogenic PAHs were found along the mid-Adriatic transect

363 (approximately 74%) and in the Kaštela Bay (61%). In the coastal sediments, contamination is

364 assigned about equally to petrogenic/pyrogenic sources of PAHs (47% and 53%, respectively),

365 whereas in Šibenik Bay a very high percentage is apportioned to the combustion compounds

366 (81%). Despite generally lower levels of petroleum hydrocarbons along the mid-Adriatic and the

367 Croatian coast (Fig. 3), these results indicate that sediment contamination by petrogenic PAHs

368 may be spatially more important. This may also be consistent with the pathways of petroleum-

369 derived PAHs, which are more dispersed, originating from various oil spillages and all routine

370 leaks that accompany diverse maritime activities (oil cargo, harbour operations, regular and

371 seasonal transport…). Whereas, the pyrogenic PAH inputs along the Croatian coast seem to be

372 more confined, being associated mainly with the urban/industrial point sources (Fig. 3). The

373 distribution of modelled concentrations of total PAHs, apportioned to three identified sources,

374 shows the peaks of high levels of petrogenic and pyrogenic PAHs, found repeatedly at the same

375 stations for all sampling periods in Kaštela Bay (station KB3 industrial port of Split) and in

376 Sibenik Bay (SB4, former ferroalloy plant, Fig. 3). Thus, it appears that contamination by PAHs

377 at these sites is not transient. The higher relative petrogenic contributions may also be seen in the

378 sediments facing the marina in Sibenik Bay (station SB1) and more generally in the whole

379 coastal area between Kaštela Bay and Dubrovnik (stations CS9, 10, 11 and 12). These areas are

380 definitely under high pressure by recreational coastal navigation. It also appears that the overall

381 source contribution determinations obtained by the ALS model compare generally very well with

382 the source indicators discussed above. The ratio of alkyl to parent PAH compounds

383 (ΣAlkyl/ΣPAH) correlates very well with the estimated percent contribution of the petrogenic

384 PAH source, thus confirming that it is an excellent proxy for these source inputs (Fig. S-5).

385   However, pure source identification might be difficult and questionable. In receptor model

386 approaches, generally, data sets do not contain end-member reference source profiles (Comero et

387 al. 2009). PAH data reflect a mixture of sources and generally no single compound is the unique

388 tracer of a particular source. Furthermore, as identified in this study, a characteristic profile of

389 PAH sources assigns very broad classes (i.e. petroleum and combustion) that to a certain degree

390 overlap in their profile identification. In addition, such PAH classes are themselves mixtures of

391 compounds derived from multiple sources. Moreover, further identification, especially of

392 combustion sources, is generally needed, in order to resolve PAHs derived from biomass burning

393 and fossil fuel (coal and petroleum) combustion. This is valuable scientific information within the

394 framework of the current efforts for global characterization of pyrogenic carbon in climate

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395   change impact studies. In sedimentary records, PAHs may be used as molecular markers, tracing

396   fossil fuel-derived pyrogenic carbon (Hanke et al. 2017). This information is also required for

397   management decisions concerning environmental measures. In the present calculations, no

398   specific PAH source markers of wood combustion were used, such as selected alkylphenanthrene

399   isomers. Likewise, certain heavy molecular weight (302 MW) compounds (known as gasoline

400   and diesel combustion markers) were not included either (Ramdahl 1983, Benner et al. 1995,

401   Allen et al. 1998, Guillon et al. 2013). The addition of such compounds would possibly help to

402   further resolve characteristic source profiles and their contributions from our set of data.

403   Additional PAH markers, which were analyzed in the Croatian sediments (such as retene, a series

404   of dimethylphenanthrenes, naphto-fluorathenes/pyrenes and dibenzopyrenes) will be used in

405   further source characterization assessments. Nevertheless, the ALS method allowed us to assess

406   the modelling power of individual compounds. The benzo[$b+j$]fluoranthenes and fluoranthene

407   and pyrene compounds characterized two combustion sources, while the alkyl-substituted

408   signature homologues (phenanthrenes/anthracenes, fluranthenes/pyrenes and chrysenes and

409   dibenzothiophenes) delineate an oil source profile. Consequently, these results provide

410   preliminary reference data for source profiles and contributions concerning the contamination of

411   marine sediment by PAHs in the mid-Adriatic and along the Croatian coast.

412   ASSOCIATED CONTENT

413   **Supporting information available**. Additional information is included for all sampling stations

414   positions and coding, PAH analyses and data, PAH concentrations and ratios, as well as

415   additional figures.

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669   **Table 1.** Summed concentration of PAHs (μg.kg^{-1} dry weight) in the surface sediments of the

670   offshore mid-Adriatic and along the Croatian coast.

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

671   Σ PAH: Sum of unsubstituted compounds phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene +
672   triphenylene, benzo[*b*]fluoranthene+ benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene, indeno[1,2,3-
673   *cd*]pyrene, dibenz[*ah*]anthracene, benzo[*ghi*]perylene.
674   Σ C-PAH: Sum of alkyl-phenanthrenes / anthracenes, alkyl-fluoranthenes / pyrenes, alkyl-chrysenes, alkyl-benzofluoranthenes,
675   Σ S-PAH: Sum of unsubstituted dibenzothiophene and three isomers of benzonaphthothiophenes.
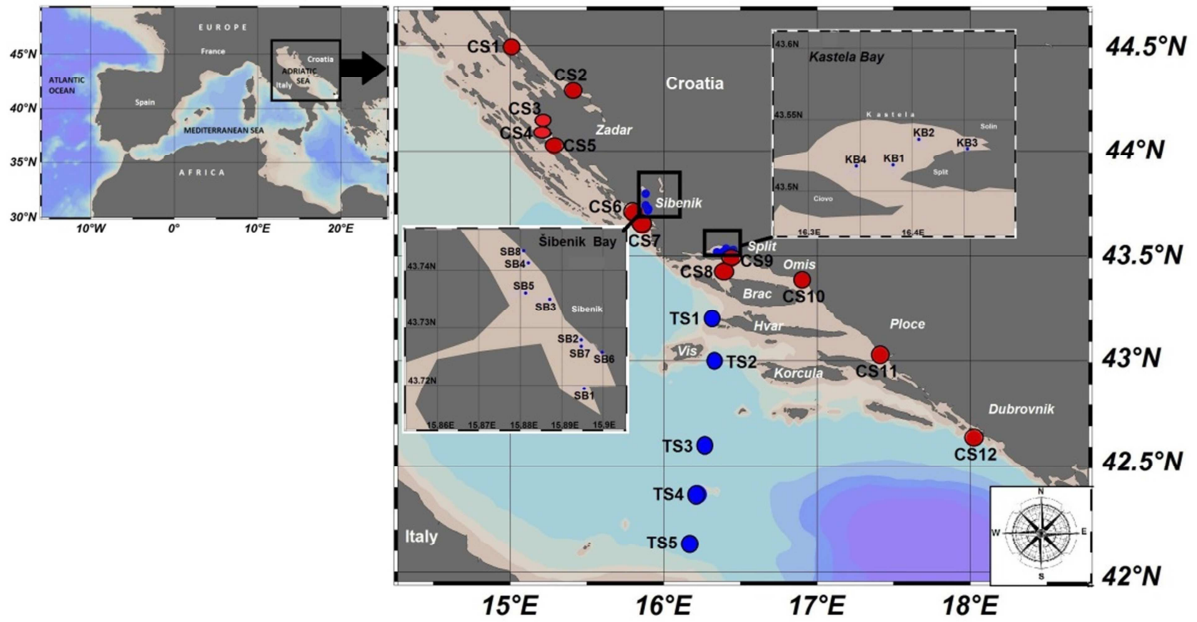676   Σ CS-PAH: Sum of alkyl- substituted dibenzothiophnes and benzonaphthothiophenes.

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Figure 1. Map showing positions of the surface sediment sampling stations in four study areas:

the mid-Adriatic transect, a coastal survey north-west – south-east, Šibenik and Kaštela bays.
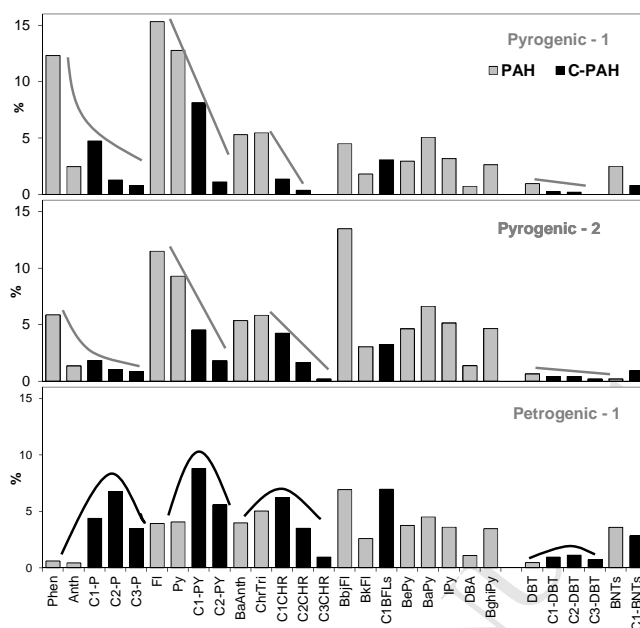
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691   Figure 2. PAH source profiles obtained by ALS Alternating Least Square calculation

692   (Pirouette, Infometrix 2014). Abundances (weight %) of parent individual compounds (PAH) and

693   of summed alkyl-substituted homologues (C1 mono-. C2 di- and C3 three-methyl substituted

694   PAH). Unresolved by GC-MS. PAH isomers are given together (triphenylene from chrysene and

695   benzo[*b*]fluoranthene from benzo[*j*]fluoranthene). For PAH abbreviations see Table S-3.

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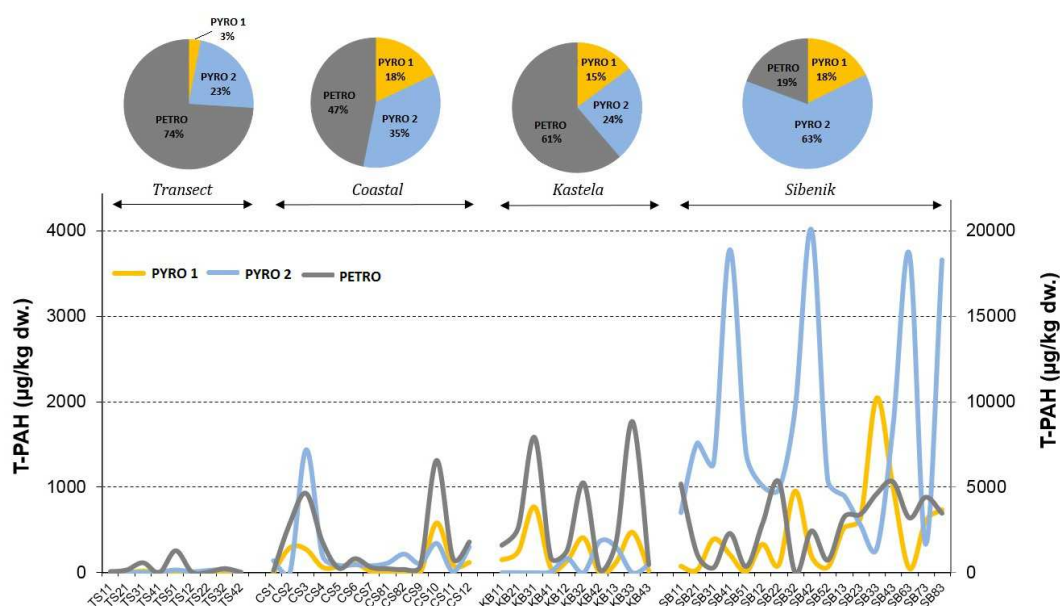
Figure 3. Distributions of modelled total T-PAH concentrations (µg/kg d.w.) apportioned into two pyrogenic and one petrogenic source in each studied area; the Sibenik Bay concentrations are given with right y-axis; Upper pies show summed weight percent of total source contributions for each area. All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

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