

# Aliphatic hydrocarbons in surface sediments of the Gulf of Trieste (northern Adriatic)—sources and spatial and temporal distributions

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## Abstract

**Purpose** A medium-term study of sedimentary aliphatic hydrocarbons in the Gulf of Trieste was performed. The content of the aliphatic hydrocarbons, including their spatial and temporal distributions and origins, was determined. The collected data on the content of these compounds for the period of 2004–2013 were then processed using different evaluation indices and statistical analyses.

**Materials and methods** Sediment samples were collected using a gravity core sampler. Hydrocarbons were extracted with hexane and dichloromethane (1:1), and their concentrations were determined by gas chromatography (using an FID detector). Principal component analysis (PCA) was performed to establish the differences between the different sampling sites.

**Results and discussion** The study's results reveal spatial and temporal variabilities in the aliphatic hydrocarbons within the investigated area. The mean concentrations of total aliphatic hydrocarbons were in the range of 17.9–84.6  $\mu\text{g g}^{-1}$  d.w., while the concentrations of *n*-alkanes from C12 to C34 were 934–5232  $\text{ng g}^{-1}$  d.w. The results of the analyses show higher concentrations of hydrocarbons in the coastal areas, with a decrease toward the central part of the Gulf of Trieste. The interannual differences in hydrocarbon concentrations were generally larger close to river estuaries and pollution sources, where degradation processes are more intensive. Different evaluation indices revealed the hydrocarbons to have different

origins. The temporal distribution of aliphatic hydrocarbons shows a decrease in concentrations over the past few years at certain sites. Important changes in the concentration and composition of the aliphatic fraction were observed in and after 2010, characterised by intensive fluvial input and long-lasting decreased salinity.

**Conclusions** The content and distribution of aliphatic hydrocarbons are largely dependent on coastal sources of these compounds. Although the investigated area could be considered only slightly to moderately contaminated by hydrocarbons, the recently applied measures for pollution reduction should be continued and intensified.

**Keywords** Aliphatic hydrocarbons · Distribution · Gulf of Trieste · Sediments · Sources

## 1 Introduction

Hydrocarbons of natural and anthropogenic origin are widespread compounds within the natural environment. The main contributors to the introduction of these compounds are oil seepage, oil spillage, urban runoff, wastewater and sewage effluents, maritime traffic, river discharges and atmospheric deposition (GESAMP 1993). The transport and distribution of hydrocarbons are dependent on hydrology, the nature and structure of suspended matter, sediment composition and freshwater inputs, among other factors. The solubility of hydrocarbons in water is very low. They are usually adsorbed on particles in the water column. The enriched suspended matter then settles onto the bottom surface sediment. In the sediment phase, the degradation of hydrocarbons is slower. Due to this, they accumulate to higher levels. Therefore, marine sediments usually contain hydrocarbons in higher concentrations than those in the water column.

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In natural marine environments, hydrocarbons usually are of different origins, which are often difficult to determine. Identification of the various sources of these compounds in a marine environment, as well as their concentrations in marine environment, is extremely important in assessing the state of the environment and planning measures for pollution reduction. This is especially important where important pollution pressure is to be expected. Different evaluation indices have been used to determine the origin of aliphatic hydrocarbons, which can be either petrogenic or biogenic (terrestrial and marine) (Commendatore et al. 2000; Readman et al. 2002; Commendatore and Esteves 2004; Darilmaz and Kucuksezgin 2007; Mille et al. 2007). These indices include the concentration of resolved and total aliphatic hydrocarbons, the presence and concentration of unresolved complex mixture (UCM), the concentrations/ratios of certain *n*-alkanes (C17, C18) and isoprenoids (pristane, phytane), the ratio between hydrocarbons with even and odd numbers of C-atoms, the carbon preference index (CPI) and the natural to anthropogenic ratio (NAR).

Aliphatic hydrocarbons usually attract less attention from researchers compared to polycyclic aromatic hydrocarbons, which are much more toxic compounds. However, aliphatic hydrocarbons are known to follow the impact of different anthropogenic activities, such as oil production and maritime traffic, and, as such, have been the focus of different studies around the world (Lipiatou and Saliot 1991; Volkman et al. 1992; Gogou et al. 2000; Mzoughi and Chouba 2011a; Mzoughi and Chouba 2011b; Gonul and Kucuksezgin 2012; Commendatore et al. 2012; El Nemr et al. 2013; Silva et al. 2014). Nonetheless, data on this subject are currently lacking for the Northern Adriatic context, with preliminary insights offered only by Bajt (2012). Therefore, the aim of the present work was to determine the content, spatial and temporal distributions and origin of aliphatic hydrocarbons in a part of the Gulf of Trieste. For this purpose, data on the content of these compounds in surficial sediments within the Gulf of Trieste from 2004 to 2013 were processed using different evaluation indices and statistical analysis. The data obtained over this 10-year period enabled me to carry out comprehensive study including temporal trends and the effects of changes to environmental and anthropogenic conditions.

## 1.1 Study area

The investigated area in the Gulf of Trieste is a part of the Northern Adriatic (Fig. 1). As this maritime area is one of the most urbanised regions along the coast of the Northern Adriatic, it is affected by pollution from different sources. For example, maritime traffic to three different ports (Koper, Trieste and Monfalcone) is intensive. These ports handle roughly 70 million t of cargo per year. The estimated annual quantity of oil and oil products carried by ships in the Gulf of

Trieste is more than 35 million t. In addition to this intensive traffic, nautical tourism is also developed, with about 15 marinas and small harbours.

The environment of investigation receives wastewater from several sewage treatment plants, as well as freshwater from rivers, which also carry industrial wastewaters. The area is rather shallow (max. depth of 25 m) and semi-enclosed, with a quite complex circulation of water masses. Its hydrological characteristics are influenced by an inflow of more saline waters from the south and freshwater inputs from the Friuli region and Carst (the Isonzo, Rizana and Dragonja Rivers; Malačič and Petelin 2009), and its water column stratification is often formed during the summer.

The mineral composition of sediment is connected to the widely distributed input of material (flysch) from the hinterland in the investigated area (Ogorelec et al. 1991). The area's clay minerals amount to roughly 30–50% of the total sediment in the bays of Koper and Piran. The amount of these minerals decreases toward the central part of the Gulf of Trieste (10–20%). The area's carbonate content (20–75%) increases moving toward the open part of the gulf (via the accumulation of skeletal matter). The amount of quartz ranges from 8 to 35%, with a decreasing trend toward the central part of the gulf. The sediment grain size is connected to its amount of carbonate fraction.

The sediments of both bays are mainly composed of silty clay (roughly 60% clay), while sand prevails in the central part of the gulf (roughly 80%), consisting mainly of biogenic detritus. The distribution of sedimentary organic carbon is connected to the sediment texture, with the former decreasing from coastal areas (1–1.5%) to the central part of the gulf (<0.5%) (Faganeli et al. 1991). The distribution could also be connected to the different sedimentation rates between the inner parts of the bays of Koper and Piran, as well as the central part of the Gulf of Trieste. The sedimentation rate of the inner parts of the bays is quite high (3–5 mm year<sup>-1</sup>), though it decreases to roughly 1 mm year<sup>-1</sup> in the central part of the gulf (Ogorelec et al. 1991). All of the abovementioned characteristics make this complex ecosystem interesting for different environmental studies.

The sampling sites are presented in Fig. 1 and Table 1.

## 2 Experimental

### 2.1 Sample collection, preparation and analyses

Sediment samples were taken using a gravity core sampler. Sampling was performed each year from 2004 to 2013 during the second half of September. The upper 2-cm layer was placed in a precleaned glass jar and frozen at -30 °C. Before analyses, the sediment samples were sieved through 250- $\mu$ m sieve to remove larger particles and then ground down.

**Fig. 1** Location of sampling sites

Roughly 10 g of sediment sample was taken for analyses, which were performed according to the UNEP/IOC/IAEA (1992) procedure. High purity hexane and dichloromethane (Fluka) were used for the extraction and separation of hydrocarbons. All other chemicals were of analytical grade, purchased from Merck and cleaned according to the procedure before use.  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were activated at 200 °C for 4 h and then partially deactivated by adding 5% of precleaned Milli-Q water. Activation of Cu was achieved with HCl. Cu was rinsed with distilled water, organic solvents and kept in hexane.

Hydrocarbons were extracted (Soxhlet) from sediment samples with a mixture of hexane and dichloromethane (50:50) for 8 h. The solution was concentrated on a rotary evaporator to about 15 ml. It was additionally concentrated under a stream of  $\text{N}_2$ . Cu powder was used to remove sulphur. The cleanup of the samples and partition of hydrocarbons into aliphatic and aromatic fractions was performed on silica and alumina using column chromatography. Aliphatic hydrocarbons were eluted with 20 ml of hexane; the sample was concentrated to roughly 0.2 ml. The concentrated samples were

analysed using an HP 6890 gas chromatograph, equipped with an HP Ultra 2 column (25 m × 0.32 mm × 0.17 μm), on column injector and a flame ionisation detector (FID). The column temperature programme went as follows: a column initial temperature of 60 °C was increased at 3 °C min<sup>-1</sup> to 290 °C, where it was maintained for 15 min. The injector temperature programme followed the column temperature programme, starting at 63 °C. The detector temperature and the carrier gas (helium) flow were 300 °C and 1 ml min<sup>-1</sup>, respectively.

Identification of resolved aliphatic hydrocarbons was performed through the comparison of retention times with those of an external standard solution of all target compounds. Concentrations of the resolved aliphatic hydrocarbons were calculated using the same external standard solution. For each sampling site, the individual *n*-alkane concentrations (C12 to C34), the concentrations of the isoprenoids pristane and phytane, the total resolved aliphatic hydrocarbons (sum of *n*-alkanes and isoprenoids), the UCM and the total aliphatic hydrocarbons (the sum of the total resolved aliphatic hydrocarbons and the UCM) were calculated for each sampling site.

**Table 1** Description of the investigated sampling sites

Site	Description	Depth (m)	Longitude	Latitude	TOC (%)
PK	Port of Koper	10	13° 44.077' E	45° 33.495' N	1.71
K	Central part of the Bay of Koper	16	13° 43.199' E	45° 33.579' N	1.28
KK	Outer margin of the Bay of Koper	21	13° 40.000' E	45° 35.500' N	0.94
CZ	Central part of the Gulf of Trieste	24	13° 37.930' E	45° 37.400' N	1.23
PM	Marina of Portoroz	10	13° 35.800' E	45° 30.400' N	1.12
MA	Central part of the Bay of Piran	16	13° 34.326' E	45° 30.009' N	1.17
F	Offshore site, 2 NM from main shipping routes	21	13° 33.000' E	45° 32.300' N	0.84

The UCM was calculated using the average response factors for aliphatic hydrocarbons. Total organic carbon (TOC) was determined on dry samples with a CHN-elemental analyser (Vario Micro Cube, Elementar, Germany) after removal of inorganic carbon (HCl). Principal component analysis (PCA) was conducted using the R statistical software package (R Foundation for Statistical Computing, Vienna, Austria).

## 2.2 Quality control and quality assurance

Quality control procedures were applied throughout the course of this study. Procedural blanks were performed together with the analyses. For recovery determination, internal standards (C19-d and C32-d) were added to each sample before the analyses. The recoveries over 10 years for C19-d were  $84 \pm 9$  and  $89 \pm 10\%$  for C32-d. Furthermore, the results were corrected for the recoveries. Limits of detection (LOD) were  $2 \text{ ng g}^{-1}$  (considering the ratio  $S/N > 2$ ). The repeatability was determined by analysing three replicates of the standard reference material. The relative standard deviations for all target compounds were below 10%. To verify the accuracy of our work, reference materials obtained from IAEA-MEL Monaco were analysed. Results were within the recommended range.

## 2.3 Evaluation indices

Natural samples are very complex. Some other parameters, in addition to absolute concentrations of aliphatic hydrocarbons, have to be applied in order to determine the probable origins. In this work, the following indices were applied:

- The low/high molecular weight hydrocarbons ratio (LMW/HMW);  $\text{LMW} \leq \text{C}20$  and  $\text{HMW} \geq \text{C}21$ ; values close to 1 have been reported for algae, plankton and crude oil, while higher plants show lower values (Colombo et al. 1989);
- The presence or absence of UCM, related to degraded/ weathered petroleum residues (Venkatesan et al. 1980), although it also can be attributed to the bacterial degradation of natural organic matter (e.g. algal detritus) (Venkatesan and Kaplan 1982);
- The pristane/phytane ratio; it is close to 1 for petrogenic hydrocarbons; biogenic hydrocarbons show higher values (UNEP/IOC/IAEA 1992);
- n-C17/Pri and n-C18/Phy; they show the presence of oil and/or the relative biodegradation of *n*-alkanes; low values are generally connected to degradation process (Colombo et al. 1989);
- The ratio between the UCM and the resolved aliphatic hydrocarbons, which is an estimation of the relative degradation rate; this is high in the case of intensive degradation processes, and values higher than 4 confirm petrogenic input (Lipiatou and Salot 1991);

- The “natural *n*-alkanes ratio (NAR)”:  $\text{NAR} = [\sum \text{n-alk}(C_{19}\text{--}C_{32}) - 2\sum \text{even } n\text{-alk}(C_{20}\text{--}C_{32})] / \sum \text{n-alk}(C_{19}\text{--}C_{32})$ , which is around 0 for petroleum hydrocarbons and crude oils and close to 1 for higher terrestrial plants and marine plants (Mille et al. 2007);
- The  $\text{CPI}_{\text{HMW}}$ , defined as  $2(\text{C}27 + \text{C}29)/(\text{C}26 + 2\text{C}28 + \text{C}30)$ ; it is around 1 for petrogenic hydrocarbons and between 3 and 6 for terrestrial plants and uncontaminated sediments (Colombo et al. 1989); and
- The  $\text{CPI}_{\text{LMW}}$ , defined as the ratio between alkanes with odd and even numbers of C-atoms (C-15 to C-22); petrogenic hydrocarbons show values around 1, with algal inputs showing higher values (Salot 1981).

## 3 Results and discussion

### 3.1 The spatial distribution of hydrocarbons

The concentrations of aliphatic hydrocarbons in the investigated area are presented in Table 2. The highest concentrations of total aliphatic hydrocarbons were observed in the Port of Koper (PK), in the middle of the Bay of Koper (K) and in the marina of Portoroz (PM). The lowest amounts were obtained in the Bay of Piran (MA) and in the area just off from Piran (F). Concentrations in the central part of the Gulf of Trieste are relatively higher than at other sites off the coast, but they are roughly two times lower than in the Port of Koper, and comparable to those in the Bay of Koper. A similar distribution pattern was observed in case of *n*-alkanes C12–C34.

Figure 2 shows the boxplots for the concentrations of total aliphatic hydrocarbons and *n*-alkanes C12–C34 from 2004 to 2013. In both cases, the range of concentrations in the Port of Koper is significantly broader, indicating significant differences of hydrocarbon input over the examined time period. Such differences could be related to changes of freshwater inflow (Rizana River) or port activities. Median concentrations and the range of concentration distribution form a decreasing gradient at the Bays of Koper and Piran. Concentrations and distribution ranges in the central part of the gulf (CZ) are comparable to those in the Bay of Koper (K). The central part of the Gulf of Trieste is influenced by the Isonzo River, as well as affected by the city and port of Trieste. The distribution ranges of *n*-alkanes and total aliphatic hydrocarbon concentrations at sites MA, F and KK are quite narrow, showing constant concentrations over the investigated time period and showing rather limited effects from coastal sources. The situation in the marina of Portoroz was somewhat surprising, as I expected a similar distribution to that found in the Port of Koper. The sites PM and PK had the following similar characteristics: a direct pollution source, limited exchange of water and the influence of river

**Table 2** Concentrations of sedimentary aliphatic hydrocarbons (ng g<sup>-1</sup> d.w.; total aliphatic and UCM in µg g<sup>-1</sup> d.w.) and different evaluation indices

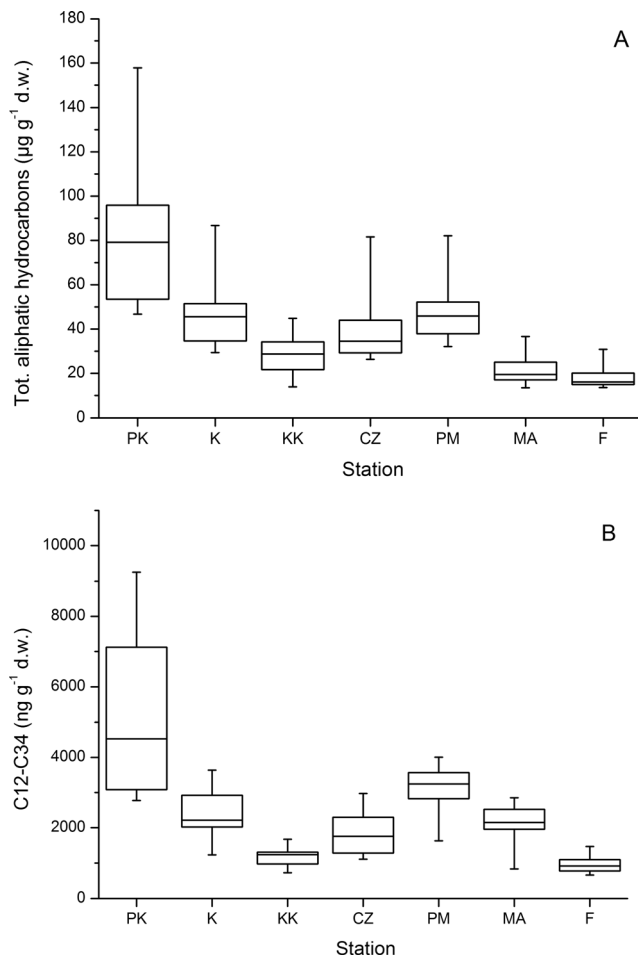
		PK	K	KK	CZ	PM	MA	F
C17	Average	108	83	39	51	569	285	51
	STD	52	37	18	16	303	132	13
Pri	Average	97	44	25	44	36	43	13
	STD	69	15	10	28	17	15	7
C18	Average	45	15	13	19	20	17	13
	STD	41	4	6	9	9	7	10
Phy	Average	54	10	6	9	39	14	4
	STD	41	5	4	5	14	7	2
C12-C34	Average	5232	2356	1182	1816	3095	2107	934
	STD	2528	724	315	609	707	576	248
R ALI	Average	5383	2411	1214	1869	3170	2164	951
	STD	2624	726	323	619	732	586	245
TOT ALI	Average	84.6	47.4	28.5	39.9	48.5	21.2	17.9
	STD	35.3	16.2	9.0	16.9	14.8	6.9	5.2
Pri/Phy	Average	2.0	4.8	5.8	5.3	0.9	3.4	3.5
	STD	0.8	1.6	2.8	1.7	0.2	1.5	1.9
C18/Phy	Average	0.8	1.8	2.2	2.3	0.5	1.3	3.6
	STD	0.3	0.9	0.8	0.9	0.2	0.5	2.2
C17/Pri	Average	1.4	2.2	1.6	1.4	17.6	7.5	10.5
	STD	1.1	1.6	0.4	0.7	9.9	3.7	18.0
UCM	Average	79.2	45.0	27.3	38.0	45.4	19.0	16.9
	STD	33.0	15.8	8.8	16.5	14.7	6.6	5.0
UCM/Res	Average	15.6	19.5	23.1	20.8	15.4	9.3	18.1
	STD	3.9	6.2	7.6	6.2	7.0	3.3	4.1
LMW/HMW	Average	0.09	0.11	0.14	0.12	0.23	0.22	0.17
	STD	0.03	0.01	0.05	0.03	0.12	0.06	0.07
NAR	Average	0.65	0.62	0.58	0.52	0.66	0.59	0.46
	STD	0.06	0.13	0.09	0.06	0.11	0.08	0.08
CPI <sub>LMW</sub>	Average	1.4	1.5	1.3	1.3	1.2	1.2	1.2
	STD	0.2	0.2	0.3	0.3	0.4	0.2	0.2
CPI <sub>HMW</sub>	Average	5.2	4.3	3.8	3.4	4.1	3.9	2.8
	STD	1.3	1.3	1.0	0.9	1.3	0.9	0.9
CPI <sub>(C12-C34)</sub>	Average	4.3	4.4	3.2	2.9	4.0	4.1	2.6
	STD	0.9	1.8	1.0	0.6	1.3	1.4	0.6

discharges. However, the distribution at site PM was more similar to that of sites K and CZ.

Aside from the influences of the inputs of these compounds from the coast, other factors can affect their distribution. For example, the sedimentation rate is higher in the inner part of both bays, leading to a higher accumulation of TOC. It has been shown that sedimentary TOC and grain size play important roles in pollutant distribution and accumulation (Readman et al. 2002). The sediment grain size in the investigated area increases toward the central part of the gulf, resulting in a lower accumulation of organic carbon. I examined the possible influence of grain size (fraction <63 µm) and TOC content on the accumulation of aliphatic hydrocarbons.

The content of resolved aliphatic hydrocarbons and TOC collected in 2008 and grain size (data from Ogorelec et al. 1991) were included in the analysis. In general, the amount of hydrocarbons was higher for sediment samples with higher TOC content and smaller grain size. However, no good linear relationship was obtained including all stations in the analysis. In the case of TOC, station PM differed significantly from the other sites, as the former was under the direct influence of hydrocarbon inputs from boats and had limited exchange of water masses, which together led to higher accumulation. Excluding this site from the calculation, a better correlation was observed ( $R^2 = 0.79$ ). A similar situation was observed in the case of the effect of grain size ( $R^2 = 0.72$ ). Station F, with





**Fig. 2** Boxplots for (a) total aliphatic hydrocarbons (µg g<sup>-1</sup> d.w.) and (b) *n*-alkanes C12–C34 (ng g<sup>-1</sup> d.w.) from 2004 to 2013

significantly lower proportion of fine sediment fraction, appeared to be an outlier. The correlation was found to be good for all other stations ( $R^2 = 0.90$ ).

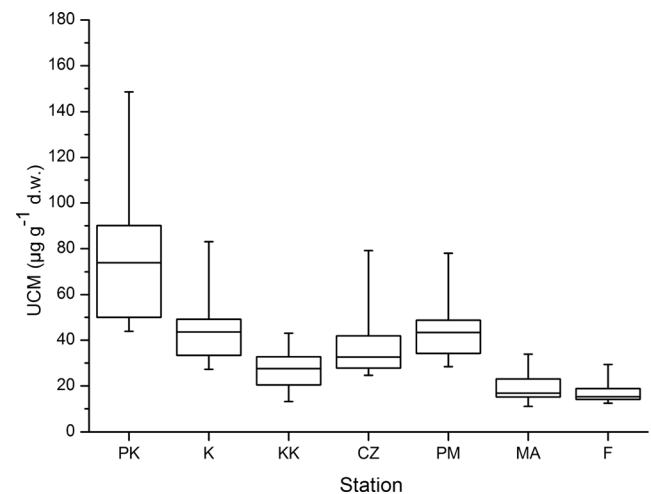
### 3.2 The origin of hydrocarbons

Aliphatic hydrocarbons are understood to come from either an anthropogenic origin or a biogenic origin. The former is usually connected to petroleum, although it can also relate to the organic materials of different origins, such as organic matter in soil and sewage. A biogenic origin can be either terrestrial (higher plants) or marine (algae and micro-algae). In complex ecosystems, it is usually difficult to distinguish between these two origins. Thus, several evaluation indices were used for this purpose. The use of data collected over 10 years enabled me to obtain greater insight into the problem of hydrocarbon sources by reducing the effects of different environmental and anthropogenic changes within a particular year.

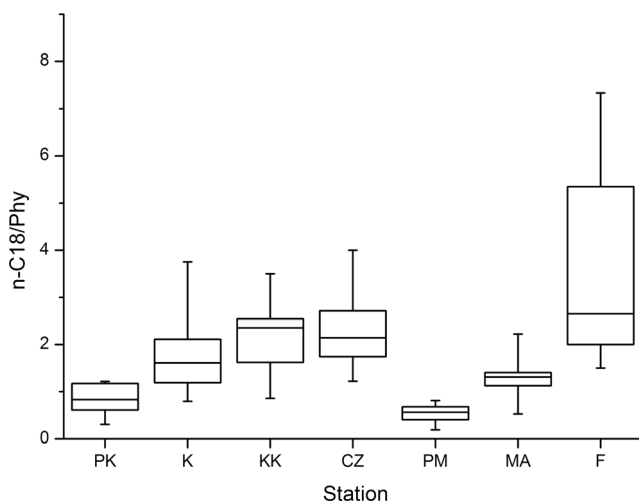
The major component of the aliphatic fractions was UCM, which was higher than 90% at all sites. UCM was detected in the range of *n*-C14 up to *n*-C34 at a maximum in the HMW

range. UCM is considered to be a mixture of branched aliphatic hydrocarbons, cyclic saturated hydrocarbons and other compounds resistant to biodegradation (Bouloubassi and Saliot 1993). It has been linked to biodegraded petroleum residues, and its relatively high content is an indication of chronic oil pollution (Yunker et al. 2002). The spatial distribution of UCM (Fig. 3) confirms important hydrocarbon sources on the coast. A continuous homologous series of *n*-alkanes from *n*-C12 was also observed at all sampling sites, indicating the existence of hydrocarbons of anthropogenic origin (Esteves et al. 2006). The calculated ratios between the UCM and the resolved aliphatic hydrocarbons were higher than 4 at all sites, which further suggests the anthropogenic origin of aliphatic hydrocarbons and important degradation processes (Gough and Rowland 1990; Gogou et al. 2000). Ratios of *n*-C17/pristane and *n*-C18/phytane are often used to assess the fresh inputs of hydrocarbons and the intensity of degradation processes. These ratios are higher in the case of fresh inputs, whereas low ratios indicate significant degradation of petroleum hydrocarbons (Colombo et al. 1989).

The isoprenoids pristane and phytane are relatively persistent compounds, and *n*-C17 and *n*-C18 are better substrates for microbial degradation. This leads to the relative increase of isoprenoid content over time. In our case, only the *n*-C18/phytane ratio was applied. The *n*-C17/pristane ratio was not suitable for use in the investigated area, because both compounds can be of marine biogenic origin in such a productive area (Saliot 1981). The lowest *n*-C18/phytane ratios were found at sites PK and PM (Table 2, Fig. 4), where a relatively higher UCM content was also detected. These two areas are rather closed off, with reduced exchange of water masses, significant freshwater inputs and, consequently, more favourable conditions for intensive degradation processes. At all other sites, the fresh input of hydrocarbons was more pronounced compared to PK and PM, where it was likely masked by intensive degradation. Comparing the boxplots



**Fig. 3** Boxplots for the UCM (µg g<sup>-1</sup> d.w.) from 2004 to 2013



**Fig. 4** Boxplots for the *n*-C18/Phy ratio from 2004 to 2013

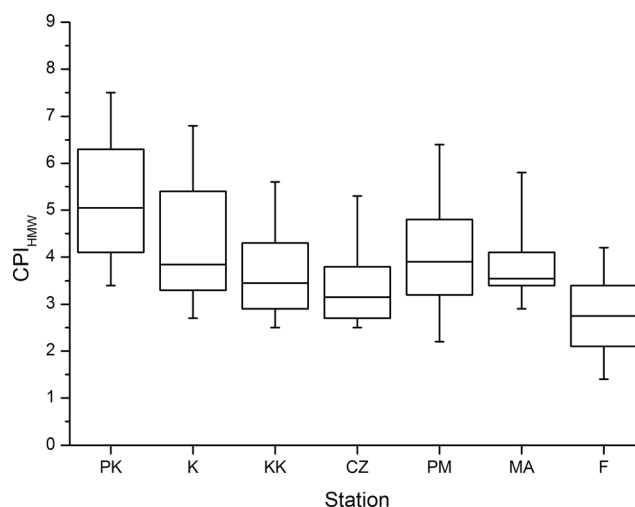
for the UCM (Fig. 3) and the *n*-C18/phytane ratio (Fig. 4), we can see a good relationship between these two parameters, with both related to the intensity of degradation processes. In general, sites characterised by higher values and broader temporal concentration ranges of UCM exhibit lower and less scattered values of the *n*-C18/phytane ratio. The boxplots show a decreasing trend for the UCM toward the offshore areas and the opposite trend for the *n*-C18/phytane ratio. The highest ratios and temporary differences in concentration distribution were observed at site F, which implies fresh hydrocarbon inputs with significant interannual differences and slower degradation processes. Regarding the position of station F (closer to the main shipping routes and more distant from the coast), maritime traffic is likely to be a significant source of aliphatic hydrocarbons in the area.

Biogenic aliphatic hydrocarbons are derived from terrigenous organic matter (plant waxes) brought into the sea by rivers or synthesised in seawater by phytoplankton and/or bacteria (Saliot 1981). Two ratios were used to evaluate the proportion of biogenic hydrocarbons, namely, the CPI (CPI<sub>HMW</sub> and CPI<sub>LMW</sub>) and the NAR. The CPI<sub>HMW</sub> typically ranges around one for petrogenic hydrocarbons and from three to six for vascular plants and uncontaminated sediment (Colombo et al. 1989), though values of up to seven have also been reported (Saliot 1981). The natural *n*-alkanes ratio (NAR) is close to zero for petroleum hydrocarbons and crude oils and close to one for higher terrestrial and marine plants (Mille et al. 2007). Strong evidence of a biogenic origin was observed in the investigated area. Aliphatic hydrocarbons with an odd number of carbon atoms from *n*-C27 to *n*-C31 were the most abundant compounds in all samples, which indicate significant terrestrial input (Saliot 1981). The CPI<sub>HMW</sub> index was higher than three at all sites save for the most distant site from the coast, F, where the impact of rivers was reduced. The distribution pattern of this index exhibited significant biogenic input by rivers. This decreasing trend from the coastal areas

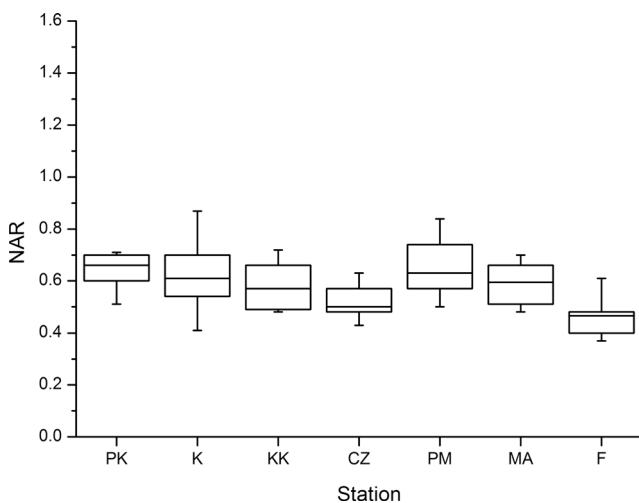
under the strong influence of freshwater input is presented in Fig. 5. The values of the CPI<sub>HMW</sub> index in this study suggest a mixed origin of both petrogenic and biogenic hydrocarbons, which appears reasonable considering the pollution sources in the investigated area.

To estimate the proportions of natural and petroleum *n*-alkanes, the NAR was calculated (Fig. 6). The highest NAR values were obtained for stations PK, K and PM (around 0.60), with the lowest value at station F (around 0.40). A slightly decreasing trend was observed in the coastal areas of both bays. According to the NAR, we can assume roughly equal proportions of both sources. The biogenic prevailed in the areas of the Rizana and Dragonja estuaries despite significant sources of pollution in these areas (port, marina), whereas the petrogenic source was more prevalent in areas distant from the coast and closer to the main shipping routes.

Hydrocarbons with more than 20 C-atoms in the molecule (HMW hydrocarbons) were more abundant than LMW hydrocarbons ( $\leq 20$  C-atoms) (Table 2). The LMW/HMW ratio was rather low, ranging from 0.09 to 0.23, and generally higher in the Bay of Piran compared to the Bay of Koper. The HMW hydrocarbons could be of either terrestrial biogenic origin or petrogenic origin (e.g. residual fuel oil from big ships or oil from tankers). The reduced incidences of LMW alkanes could be due to the intense degradation of these compounds. To additionally confirm the presence of petrogenic hydrocarbons in the investigated area, I analysed a sediment sample from the outer margin of the Bay of Koper, as well as very close to the main shipping route to the Port of Koper (i.e. an area in the middle between site K and KK). This analysis revealed a pronounced petrogenic origin of hydrocarbons. The sample was characterised by a resolved hydrocarbon content of 3435 ng g<sup>-1</sup> d.w., a relatively high LMW/HMW ratio (0.32), a significant UCM content (88 μg g<sup>-1</sup> d.w.), a rather low CPI<sub>HMW</sub> (1.5), a very low NAR (0.07), an *n*-C17/Pri ratio of



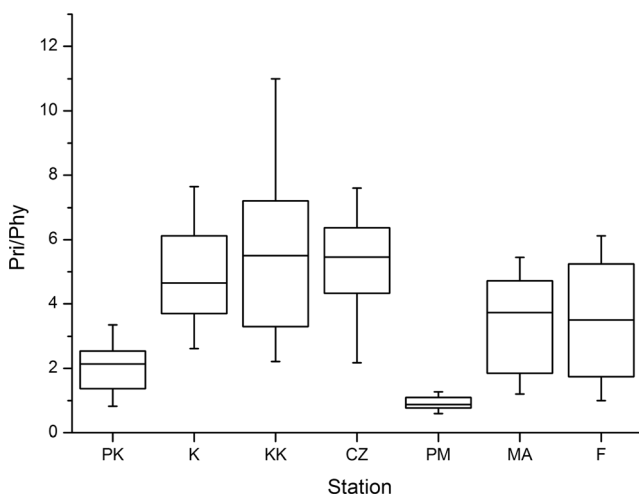
**Fig. 5** Boxplots for the CPI<sub>HMW</sub> from 2004 to 2013



**Fig. 6** Boxplots for the NAR from 2004 to 2013

2.1 and an n-C18/Phy ratio of 3.3. These values clearly speak to a substantial contribution of hydrocarbons of petrogenic origin.

In the range of LMW hydrocarbons, those of the petrogenic origin were more evident. This was confirmed by the CPI in the LMW range ( $CPI_{LMW}$ ), which was closer to one (Table 2). The biogenic and/or petrogenic contribution was determined via the pristane/phytane ratio. Although both pristane and phytane can be found in weathered petroleum products (Broman et al. 1987), pristane in higher concentrations is more likely connected to marine biogenic sources, such as phytoplankton and zooplankton (Broman et al. 1987; Saliot 1981). My results showed rather high Pri/Phy ratios save for at sites PK and PM, where the differences between different years were quite small. These low Pri/Phy ratios at sites PM and PK confirm the significant contribution of the petrogenic source, which can be connected to the direct pollution of ships and boats in the port and marina. At all other sites, the Pri/Phy values and their scattering were higher (Fig. 7), which can be



**Fig. 7** Boxplots for the Pri/Phy ratio from 2004 to 2013

connected to greater biological production and its environmental influences during the study period.

A marine input from macro- and micro-algae was also evident from the relatively high concentrations of heptadecane (n-C17; Saliot 1981). These were especially high in the Bay of Piran and relatively high in the Port of Koper. This high heptadecane concentrations are not really in accordance with the values of the Pri/Phy ratios, which were the lowest at sites PK and PM. Considering this, we can assume that pristane was more likely of petrogenic than biogenic origin in this case, which also confirms the prevailing petrogenic origin of LMW hydrocarbons.

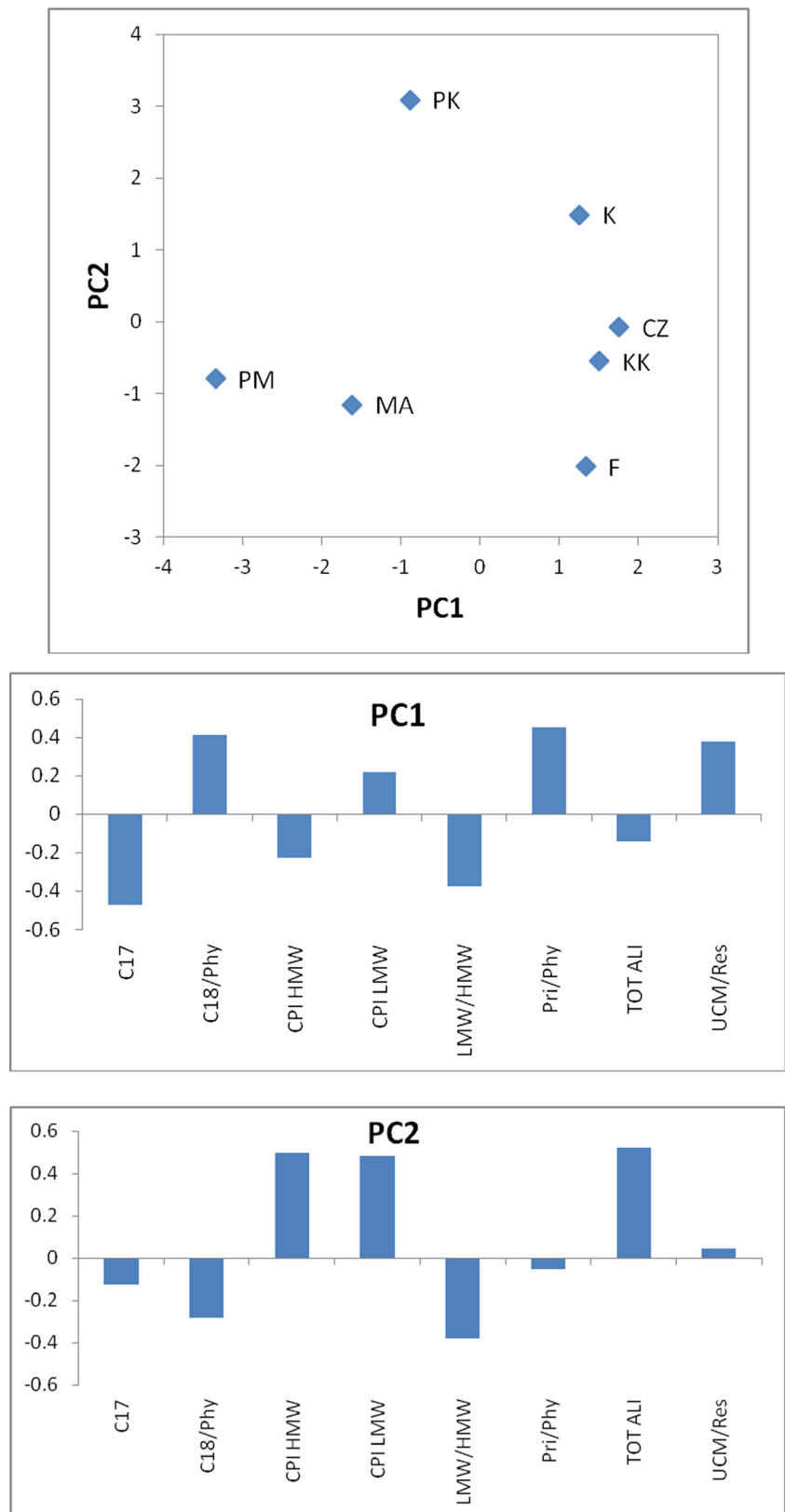
### 3.3 Differences between sampling sites

The data presented in this work speak to certain differences between sampling sites. In general, the coastal sites differ in hydrocarbon concentration and composition from sites more distant from the coast. The semi-enclosed area of study, with its complex water circulation, various sources of pollution and freshwater inputs, is quite complex. Aliphatic hydrocarbons can derive from different sources (anthropogenic, biogenic, terrestrial, marine), with interannual differences related to changing environmental conditions.

To obtain greater insight into the differences in hydrocarbons composition and distribution, the variability of the studied sampling sites was explored statistically using PCA. Standardised values of total aliphatic hydrocarbon concentrations, heptadecane (n-C17) and different evaluation indices were included in this analysis. The factor loadings and scores of the PCA analysis are presented in Fig. 8. The first PC accounted for 48% and the second for 38%. Together, they explained 86% of the total variance. Based on these two components, the sampling sites were quite scattered, with only sites KK and CZ, which had the highest positive PC1 loadings, showing certain similarities. These sites in the northern part of the gulf and more distant from the coast had few distinct characteristics. They were characterised by relatively low content of aliphatic hydrocarbons, of somewhat prevailing marine biogenic origin (higher Pri/Phy) and of rather intense degradation processes (higher UCM/Res). Site K in the central part of the Bay of Koper had positive PC1 and PC2 loadings. Concentrations of total aliphatic hydrocarbons were relatively higher, with important degradation of hydrocarbons (higher UCM/Res), and the biogenic origin of hydrocarbons (terrestrial and marine) was even more pronounced (higher Pri/Phy,  $CPI_{LMW}$  and  $CPI_{HMW}$ ). These characteristics became more concrete at site PK in the Port of Koper, which had the highest positive PC2 loading. The concentrations of total aliphatic hydrocarbons at this site were the highest in the investigated area; the biogenic origin (terrestrial and marine; higher  $CPI_{LMW}$  and  $CPI_{HMW}$ ) was even more pronounced (the Rizana River), although the petrogenic origin was also



**Fig. 8** Results of the principal component analysis for the aliphatic hydrocarbons in sediment samples



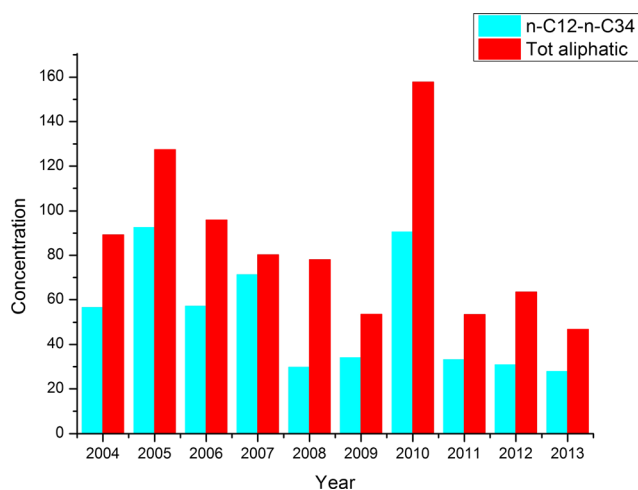
important (low Pri/Phy), and the degradation processes of hydrocarbons were quite intense (low C18/Phy). The two sites in the Bay of Piran (MA, PM), with their negative PC1 and PC2

loadings, differed significantly from those in the Bay of Koper and the central part of the Gulf of Trieste. Site MA was characterised by lower concentration of aliphatic

hydrocarbons, lower degradation (lower UCM/Res) and a greater proportion of LMW hydrocarbons of predominantly petrogenic origin (lower  $CPI_{LMW}$  and Pri/Phy). A similar situation was observed at site PM, but the concentration of aliphatic hydrocarbons here was higher and petrogenic origin was even more significant (low Pri/Phy). These two sites also showed the greatest contribution of hydrocarbons of marine biogenic origin (*n*-C17). The Bay of Piran is under the influence of the Dragonja River and significant nutrient loads from an agricultural area. Moreover, mussel and fish farms are situated in this area, representing additional sources of organic matter and nutrients. Site F, the most distant from the coast, differed from the other sites in terms of high positive PC1 loading and the highest negative PC2 loading. It was characterised by the lowest concentration of total aliphatic hydrocarbons, rather slow degradation (higher C18/Phy), and hydrocarbon inputs of mixed origin, with a significant proportion of petrogenic origin (lower  $CPI_{HMW}$  and  $CPI_{LMW}$ ). Site F is namely not far from the main shipping routes to and from the three ports in the gulf.

### 3.4 Temporal distribution of aliphatic hydrocarbons

The dataset collected during the 10-year monitoring of sedimentary aliphatic hydrocarbons in the investigated area was also used to establish their temporary distribution. For this purpose, total aliphatic hydrocarbons and *n*-alkanes C12–C34 were included in the analyses. Data on river discharges (Environmental Agency of Slovenia) and the number of ships in the Port of Koper over this time period were also considered. The situation in 2010, which will be discussed below, was very different (river flows, salinity) compared to other years. Therefore, this year was removed from the analyses. In general, no important trends were detected, although certain alterations of hydrocarbon content were observed at specific sites. The most significant change in this regard was detected at the Port of Koper, where the data showed two levels of concentration (Fig. 9), with the concentrations of *n*-alkanes C12–C34 up to two times lower following 2007. A similar situation in the port, though 1 year later, was observed in relation to total hydrocarbons. This change could be connected to a drop in fluvial input and/or changes in port activities. The Rizana River flow changed over the study's 10-year period, and it was much higher in 2008, 2009 and 2010 than in previous years (Table 3). This did not, however, lead to a higher  $CPI_{HMW}$  index (indicator of terrigenous origin), as it was even lower (between 3 and 4) compared to the period before 2008 (between 4.7 and 6.3). In addition, the number of ships in the port decreased by nearly 20% from 2008 due to the world economic crisis, which could be one of the reasons for the lower amount of aliphatic hydrocarbons after 2007. The Rizana River also brings waters from a sewage treatment plant in its estuary into the port area. This plant collects runoff



**Fig. 9** Temporary distribution of total aliphatic hydrocarbons ( $\mu\text{g g}^{-1}$  d.w.) and *n*-alkanes C12–C34 ( $10^{-2}$  ng  $\text{g}^{-1}$  d.w.) in the sediment samples from the Port of Koper

waters from the city of Koper, and the plant included only a primary treatment step. The sewage treatment plant was reconstructed in 2008 to 2009, and now, the sewage is treated with much higher efficiency. A part of the detected decrease in concentrations after 2007 could be also attributed to the inputs in the previous 2 or 3 years if we consider the sedimentation rate in the Port of Koper (at least  $5 \text{ mm year}^{-1}$ ). The study period was characterised by the continuous implementation of measures for better environmental management in the Port of Koper. For example, many new systems (with oil traps) for the collection of runoff waters from the surfaces of the port were built, and these systems are cleaned properly and frequently.

At all other sites, no drop in hydrocarbon concentrations was detected, although reduced concentrations of resolved *n*-alkanes were observed during the last 3 years of study in the Bay of Koper and the Bay of Piran, as well as in the central part of the Gulf of Trieste. In addition to the increase in environmental awareness over recent years, the reduced concentrations could be due to lower cargo throughput in the Port of Koper and less intensive nautical tourism since 2008.

Extremely different compared to other years of the study period, 2010 was characterised by increased river flows in the investigated area (Cozzi et al. 2012). Indeed, the results presented by Tinta et al. (2015) show pronounced flow from the Po river mouth (by far the biggest river in the Northern Adriatic) toward the Istria peninsula. A portion of the Po water outflow was transported north-eastward to the Gulf of Trieste, where it affected only the latter's outer part.

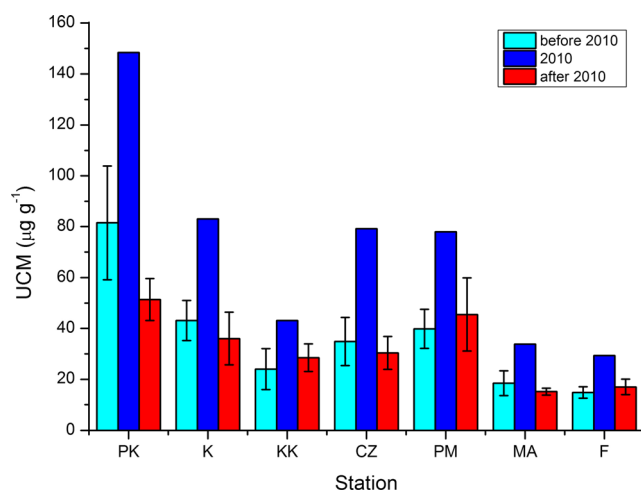
For the purposes of this study, I compared the Isonzo, Rizana and Dragonja River flows (Table 3). The Isonzo River is the major river in the gulf, with the contribution of the other two rivers amounting to less than 10%. However, the latter nonetheless have a degree of impact on the Bay of Koper and the Bay of Piran, respectively. The river flows in 2010 were found to be roughly two times higher than the average

**Table 3** The average flow of rivers in the investigated area ( $\text{m}^3 \text{s}^{-1}$ ) (Slovenian Environment Agency; Regional Agency for Environmental Protection, Emilia Romagna, Italy)

River/year	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Rizana River	3.6	3.0	3.5	2.5	3.8	3.9	6.5	1.9	2.1	5.3
Dragonja River	0.7	0.6	0.9	0.5	0.9	1.0	2.4	0.5	0.3	1.4
Isonzo River	–	55.8	68.0	59.6	108.0	111.0	143.0	78.1	96.2	122.0
Po River	1217	822	796	717	1522	1770	1910	1370	1150	1820

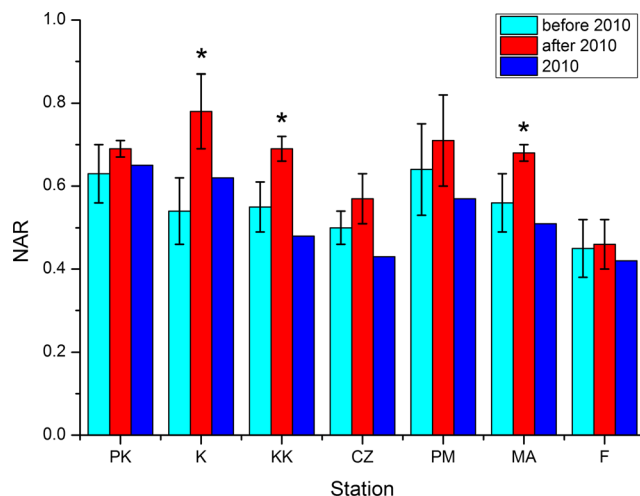
flows in other years (Table 3). It should be mentioned that in 2008, 2009 and 2013, river flow was also increased, but the difference was roughly two times lower than that in 2010. Another very important difference in 2010 was the salinity of the surface seawater. The salinity of the investigated area is usually around 37. In spring/late spring, this often decreases to 36 (or even 35) due to greater fluvial input, but rarely drops below 35. The drop in salinity also occurred in the abovementioned years, but decreased salinity was detected only for 1 to 2 months.

In 2010, the situation was very different. The salinity of surface water in the Gulf of Trieste was much lower, sometimes even below 30. In addition, this decreased salinity was detected from May to November. These differences were tied to changes of sedimentary hydrocarbon concentrations. In 2010, increases in concentrations of resolved *n*-alkanes, *n*-C17, pristane and, especially, UCM were observed (roughly two times higher) (Fig. 10). In general, the highest concentrations of hydrocarbons were seen at sites close to river estuaries, with relatively high concentrations in coastal areas and in the middle of the Gulf of Trieste, and then decreasing toward the offshore areas. This situation was unambiguously connected to the increased input of riverine water. In the case of *n*-C17 and pristane, the higher biological productivity of the area was most likely related to the increased input of nutrients from rivers. Higher chlorophyll *a* concentrations were observed

**Fig. 10** Change of UCM concentration in 2010

during this period (Talaber et al. 2014). Increased *n*-C18 and phytane concentrations were also observed, but this was limited to the Port of Koper. I expected an increase in the  $\text{CPI}_{\text{HMW}}$  and NAR, as these ratios are an indication of terrestrial biogenic hydrocarbon input. Elevated ratios were detected 1 year later and were generally higher until 2013.

A two-way analysis of variance (ANOVA) was performed to explore the differences between two time periods, namely, before and after 2010. A general comparison for all investigated sites revealed a statistically significant difference ( $p < 0.01$  for  $\text{CPI}_{\text{HMW}}$  and NAR). The comparison of individual sites in terms of NAR is presented in Fig. 11. The most significant changes could be seen at sites in central parts of the bays and the gulf, while for the most distant site from the coast, F, almost no difference was found. These results show part of the terrigenous hydrocarbons to be associated with the fine fraction of suspended matter. The sedimentation of these adsorbed hydrocarbons is slower, and they spread by surface water masses of lower salinity. In contrast, the organic matter associated with larger suspended particles was found to settle down to the sea bottom faster during times of the increased river input. The result of this was a nearly simultaneous increase in UCM, especially in areas close to the river mouths (Fig. 10). While hydrocarbons associated with the fine particle fraction reached more distant areas, their impact on the

**Fig. 11** NAR before and after 2010 (asterisk indicates statistically significant differences)

composition of aliphatic fractions emerged after a certain amount of delay. This was especially evident in the central part of both bays and the gulf after 2010, when the NAR exceeded the value of 0.7 (and even 0.8 in some cases). As we moved closer to the offshore areas, this impact became less significant, indicating a rather limited transport of organic matter to the outer margin of the Gulf of Trieste.

The presented results speak to the complexity of the semi-enclosed water system of study, including its complex circulation of water masses and variety of influences from different input sources. The current composition and distribution of hydrocarbons were found to be dependent on different conditions (e.g. water circulation, hydrocarbon spreading, sedimentation, degradation). Therefore, further medium-term studies can gather additional data on this area for better assessment of the state of such marine environments. Such studies can also work to establish the boundaries between different levels of contamination. In this case, a boundary for heavily contaminated sediment by total aliphatic hydrocarbons could be set at  $100 \mu\text{g g}^{-1}$  d.w., with moderately contaminated sediment including concentrations in the range of  $30\text{--}100 \mu\text{g g}^{-1}$  d.w., and concentrations below  $30 \mu\text{g g}^{-1}$  indicating slightly polluted or uncontaminated areas. These boundaries are higher compared to those that have been set for the open sea (Readman et al. 2002), especially for slightly contaminated sediment.

#### 4 Conclusions

The spatial distribution of the aliphatic hydrocarbons in the Gulf of Trieste was related to the examined area's distance from the coast. The highest concentrations were found in coastal areas, with a decreasing gradient observed toward the offshore areas, indicating significant sources of these compounds on the coast.

According to certain evaluation indices, both anthropogenic and biogenic sources could be found in the investigated area. The biogenic sources of fresh inputs, especially the terrigenous ones, appeared to prevail in general, though a significant proportion of fresh inputs could be assigned to petrogenic hydrocarbons. UCM was the major component of the total sedimentary aliphatic hydrocarbons, indicating substantial petrogenic inputs and intensive degradation processes. Relatively higher concentrations of n-C17 and pristane indicated the marine input (plankton).

The temporal distribution of aliphatic hydrocarbons in the Gulf of Trieste did not show significant general trends. The most evident decrease in hydrocarbon concentrations was observed in the Port of Koper. This change was reflected in a less expressed decrease of concentrations at areas on the transect to the central part of the gulf. Significant changes in the concentration and composition of the aliphatic fraction were observed both during and after 2010, the year characterised by

unusually intensive fluvial input and decreased surface salinity for more than 6 months. These changes indicated differences in transport of suspended matter of different sizes with adsorbed hydrocarbons. The results of the present study confirm the complexity of semi-enclosed marine areas that are subject to sources of pollution and freshwater discharges. The investigated area could be generally considered as slightly to moderately contaminated by hydrocarbons.

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