



# How building an underwater pipeline connecting Libya to Sicilian coast is affecting environment: polycyclic aromatic hydrocarbons (PAHs) in sediments; monitoring the evolution of the shore approach area of the Gulf of Gela (Italy)

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## ABSTRACT

The purpose of this study was to determine the variation of concentrations and distribution of PAHs in the sediments of the Gela coastal area (Italy) caused by the construction of an underwater pipeline connecting Libya to Sicilian coast. The receiving terminal of offshore pipeline, crossing the Mediterranean Sea, 516 Km long, up to 1127 meters deep, is located in Gela (Sicily, Italy). No bibliographic data regarding hydrocarbons are available for this area. In this paper we report the results of analysis on the water and organic along PAHs. The total concentrations of 16 PAHs in the sediments, analyzed during five surveys, ranged from 2.4 to 434  $\mu\text{g}/\text{kg}$  of dry weight. The highest concentrations of total PAHs were found in sediments during the monitoring campaign immediately following the laying of the pipeline. A progressive decrease during the subsequent surveys was observed: The found concentrations was in the direction of restoring the initial situation. Highest levels of PAHs concentration have been often observed in sample stations endowed with highest organic matter content.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are semi volatile and persistent organic compounds of great concern, due to their wide distribution in the environment and to the toxic and carcinogenic properties of many of them. [1–6].

The interest in PAHs, both from the analytical and environmental point of view, lies with the fact that, although most of them have no practical use, they are widespread in all the environmental compartments. PAHs are ubiquitous contaminants [7–15] that have been released into the environment through industrial processes such as wood treatment facilities, household heating, road transport [16] and manufactured gas plant sites [17]. They can be found, with different levels of concentration, in atmosphere [18], water [19], soil [20,21], sediments [6,22–27], food [14,15] and several different matrices [13].

PAHs can enter into aquatic ecosystems through natural and anthropogenic sources. The non-point sources are diffuse and disseminated through the air and waterways. As a consequence of their hydrophobic nature, PAHs in aquatic environments rapidly combine with particulate matter, may settle to the sea's bottom under calm conditions and accumulate in sediments. In

the dark and in anaerobic conditions they are very persistent [28,29].

Sediments therefore represent the most important reservoir of PAHs in the marine environment. Once PAHs enriched particles accumulate in sediments they may undergo a number of changes caused by chemical or microbial activities. As a result, the bound PAHs can be remobilized from the sediment into the water phase. Some PAHs, persistent and toxic to aquatic organisms, tend to bioaccumulate. This can cause acute or, sometimes, chronic effects on fish, birds and other mammals that feed themselves on aquatic organisms [30–32].

In the past few years, much work has been carried out into identifying sources of PAHs in sediments [6,8,16,22–27,33]. PAHs sources can be divided into three main classes according to their characteristic fingerprints. One important input of PAHs into the marine matrices is from pyrogenic sources, i.e. the combustion of organic matter, anthropogenic industrial activities, or natural and malicious fires. These sources give rise to complex mixtures of PAHs characterized by a high abundance of parent PAHs and a low proportion of alkylated PAHs. The second group is petroleum hydrocarbons from petroleum transportation, off-shore exploitation, oil spills or natural oil seeps. The composition of petroleum hydrocarbons is very complex and characterized by a high abundance of alkylated PAHs. Finally, a few compounds may have a diagenetic origin. Most frequently detected, perylene can be derived from biogenic precursors. Reducing sediments, which

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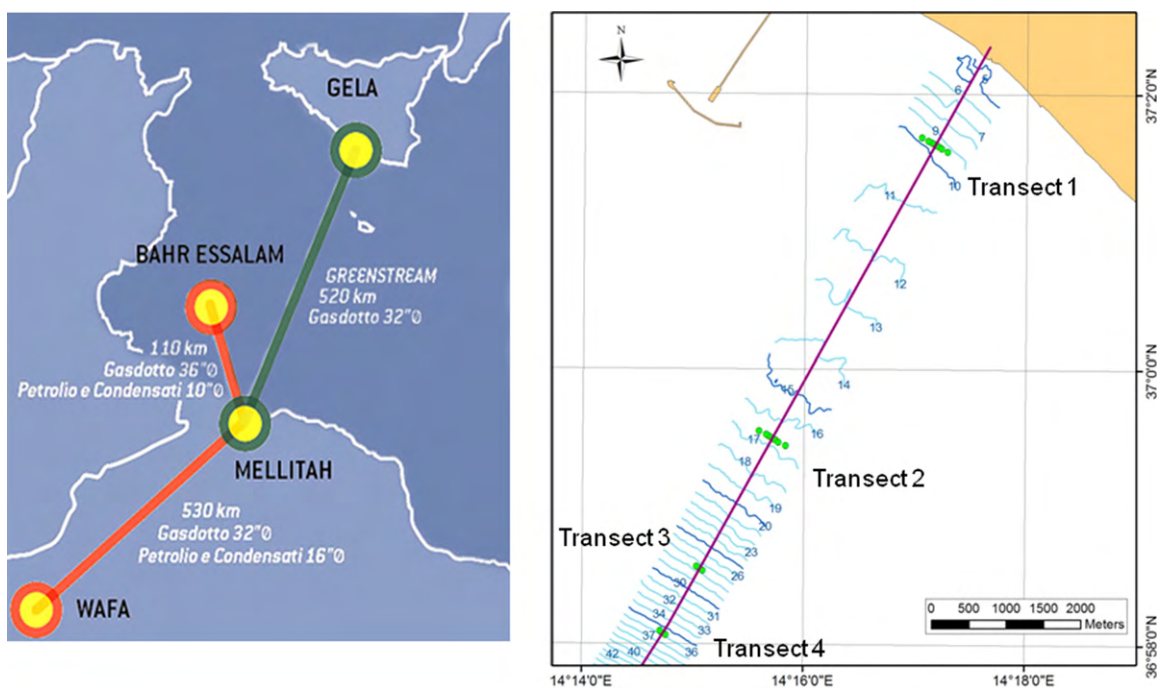


Fig. 1. Investigated area and location of sediment samples.

receive significant amounts of terrestrial organic matter, contain relatively high amounts of perylene. Perylene could also derive from aquatic material or diatoms and combustion processes [34].

Different sources (pyrolytic, petroleum and diagenetic hydrocarbons) give rise to different typical PAHs patterns and it is therefore possible to estimate the major processes that generate these compounds [35].

According to the permits granted by the competent authorities, a marine environment periodical monitoring of the Italian shore approach of the sealine connecting Libya to Sicilian coast in Gela (Sicily, Italy) have been set up.

The GreenStream System conveys dry and sweet natural gas from coastal facilities in Libya to Italy, via an offshore pipeline, with associated initial gas compressor station and a receiving terminal. The GreenStream System is part of the Western Libya Gas System, which includes:

- a gas compression station at Mellitah, aside the Gas Treatment Plant, that compresses the Gas to be exported, up to the pressure required for the export to the Italian Gas Transport Network;
- a single 32" ND Offshore Pipeline, 516 km long, to export the gas from Mellitah Gas Compressor Station to Sicily (Italy). The maximum water depth along the route is 1150 m;
- a single 32" ND offshore spur, 7.4 km long, laid in the Sicilian shore approach from the Receiving Terminal to a water depth of 19.5 m;
- a Receiving Terminal in Gela, to receive the gas from the offshore pipeline and to let it into the Italian Gas Transport Network.

Since the 1960s, pipelines development in the world captured the public awareness to environmental protection. The complex operation to build a pipeline, is associated to both technical problems and significant environmental challenges, and also casts short- and long-term ecological, sociological, economic and aesthetic adverse impacts to the region along the route.

Since there are no previous data concerning the concentrations of PAHs in the sediments of Gela coastal area, which represents ten kilometres of coast on which industrial, nautical, harbor and tourism activities can be found and, as a result of the fact that some environmental groups argue that the construction of an underwater pipeline could cause the deterioration of environmental quality, in this study the influence of the underwater construction of the pipeline connecting Libya to Sicilian coast was examined. In particular, the variation of concentrations and distributions of PAHs in the sediments of the Gela coastal area was studied.

PAHs, water and organic contents were analyzed in samples collected in two surveys, because it has been demonstrated that the concentrations of PAHs in sediments are often affected by the chemical composition of the samples such as organic matter and water content [8,27].

Investigations have been performed on fifteen PAHs recommended by US-EPA as priority pollutants to be monitored in the framework of the environmental quality control [4,5]. Several PAHs compounds have been classified into potential (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer [5]. Moreover, perylene, non US-EPA listed PAHs, has been investigated with the view to obtain additional information on PAHs origin.

## 2. Materials and methods

### 2.1. Site

The area of Gela is placed along the Mediterranean southern coast of Sicily (Fig. 1). Gela's economy relies mainly on the ENI-AGIP petrochemical complex, some allied mechanical industries and agricultural activities are also present.

The investigated marine area is a proper belt from shore to 25 Km along the pipeline route (i.e. the limit of Italian territorial sea water 120 meters deep).

#### Table 1.

Moving from coast off the shore, the investigated marine area is mainly characterized, by sands, muddy sands and muds. Sandy



acetone (analytical grade) respectively. These were finally baked in the oven at 110 °C overnight. To avoid contaminations of samples, different glassware and syringes were used for standards and solutions extracted from samples.

#### 2.4.3. Quality assurance

Various techniques and solvents were tested in order to identify the most efficient extraction procedure. Different recovery tests were carried out [21–23]. The results evidenced the Soxhlet as the better method because of the highest percentage of PAHs ( $84 \pm 8\%$ ) recovered, which is in accordance with literature data [22,37,38].

The analytical technique was preliminarily tested in order to identify the efficiency of the preparation and extraction procedure. The test was carried out by using samples without polycyclic aromatic compounds. These three “blank” samples were obtained through several extraction steps in 48 hours [21–23]. After the complete PAH extraction was carried out (checked through GC-MS analysis), a known amount of PAH (EPA) standard mixture was added to each blank sample.

The test-samples obtained in this way were extracted using the above mentioned method (Soxhlet extractor for 24 h using a dichloromethane-pentane 1:1 v/v). The total PAH concentrations were calculated for the investigated compounds, and recovery ranged from 75 to 102%. The results showed that the Soxhlet method allowed a good PAH recovery with small standard deviations (average 8%).

In addition, the accuracy of the method was assessed by analyzing a Standard Reference Material (freshwater harbour sediment BCR 535 by IRMM). The recovery (yield on the certificate value  $\pm$  RSD) for four replicates were: Pyr,  $88.0 \pm 8.5$ ; BaA,  $113 \pm 9.1$ ; BaP,  $105 \pm 9.0$ ; BbF,  $102 \pm 7.2$ ; BkF,  $81.9 \pm 6.9$ ; InP,  $102 \pm 6.3$ , respectively.

Recoveries of the surrogate standards (anthracene- $d_{10}$  and benz[*a*]anthracene  $d_{12}$ ), added before the extraction procedure, were calculated. The results for the analyzed compounds ranged from 72 to 103%.

Four deuterated PAH standards (acenaphthene  $d_{10}$ , phenanthrene  $d_{10}$ , chrysene  $d_{12}$  and perylene  $d_{12}$ ) were added as internal standard to each extract prior to the GC-MS measurements.

The calibration was performed once a week. Relative standard deviations of the three PAH analyses ranged from 7% to 16%.

The compound-specific coefficient of variation (as a measure of analytical precision) was within 4%, based on 3 injections of the standard solution. A blank (cartridge without sample) was run up every 5 samples. All the reported data were blank corrected.

The detection limit (LOD), estimated as  $3\sigma$  (three times the background noise) (IUPAC criterion), was similar for all analyzed compounds and results were less than  $0.0033 \mu\text{g}/\text{kg}$  d.w. for all analytes.

The blank values of analytical procedure remained always below the quantification limit (LOQ):  $0.01 \mu\text{g}/\text{kg}$  d.w., estimated as 10 times  $\sigma$ . Reproducibility of analyses was tested by three replicate analyses of sediments; it ranged from 3.2% to 20% of relative standard deviation.

#### 2.4.4. PAHs Extraction

All samples, dried at room temperature in darkness, were extracted in a Soxhlet extractor for 24 h using a dichloromethane-pentane 1:1 (v/v) solvent mixture. The extracts were filtered through a pre-cleaned Pasteur pipette filled with solvent-rinsed glass wool and pre-cleaned anhydrous sodium sulphate, previously rinsed with dichloromethane and concentrated in a rotary evaporator with thermostatic bath at ( $T = 35 \pm 0.5$  °C). The final volume was around 2 mL. The last stage in the procedure involved drying the solution containing PAHs under a weak nitrogen flow at room temperature. The dry residue was dissolved in 0.25 mL of a

solution containing the following perdeuterated internal standards in cyclohexane (0.2 mg/L each): acenaphthene- $d_{10}$ ; phenanthrene- $d_{10}$ , chrysene- $d_{12}$  and perylene- $d_{12}$ .

#### 2.4.5. PAHs analysis

PAHs were analyzed with a gas chromatograph (Shimadzu mod. GC-17A) equipped with a mod. GCMS-QP5000 mass selective detector (GS/MS) using a  $30 \text{ m} \times 0.25 \text{ mm}$  (i.d.) SLB<sup>TM</sup>5MS fused-silica capillary column from Supelco (Milano, Italy) and operating in the selected ion monitoring (SIM) mode.

The injector mode was splitless (0.61 min) and a total flow of 20.6 mL/min was used. The injection of both extracts from samples and standard solutions ( $1 \mu\text{L}$ ) was performed by hand. The injector temperature was maintained at 280 °C. The GC temperature program was: from 60 °C (2 min) to 325 °C at 14.5 °C/min. The carrier gas was helium (flow rate 1.4 mL/min) and the interface temperature 300 °C. Analysis was performed in Selected Ion Monitoring (SIM) mode. Identification of the components of the standard mixture was carried out by comparing retention times for each component in the mixture with those of pure components analyzed under the same experimental conditions. Identification was confirmed by comparing the spectra of the single components with those stored in the library acquisition system. The identification of PAHs in the extracted solutions was carried out on the basis of previously determined retention times and confirmed using mass spectra.

The PAHs content in the sample was quantified relative to the perdeuterated PAHs added to the dry residue. The response factors for different compounds were measured by injecting a mixture containing standard compounds and having the same concentration of perdeuterated PAHs as used for spiking the sample.

The most abundant ion was used for quantification and two other ions were additionally used for confirmation. The list of formed groups of PAHs, the deuterated standards employed, the quantification ion and the confirmation ion for each PAH are reported in our earlier works [7,8,11–15].

#### 2.5. Water content analysis

About 2 g of previously centrifuged at 4000 rpm for 10 min (Centrifuge ALC mod. 4218) sediment was dried at 105 °C for one night. The water content was determined by the weight loss and utilized to correlate all the results with dry weight. Reproducibility of water content (RSD = 3.8%) was tested by four replicate analyses of samples.

#### 2.6. Organic matter analysis

Total organic matter in soil was determined by ignition. This procedure is known to over-estimate the organic content, due to the elimination of carbonates, so the analyses were carried out only on samples deprived of carbonates content. A dried sample aliquot (2–3 g) was weighed in a platinum crucible and then carbonate was removed by treating the sample with 10% (v/v) HCl. Afterward the samples were dried at 60 °C in an oven and the content of total organic carbon (TOC) of the soil was measured by determining the loss of weight after combustion at 550 °C for 4 hr.

In order to verify the accuracy and the reproducibility of the analytical procedure, an experiment was carried out (at least three-fold replicates) by using dried at 550 °C for 12 hr samples added of known quantities of phenanthrene (a reference certified standard of sediment containing the organic matter was not available in the laboratory). Considering the mean value of three analysis, accuracy was about 96% and reproducibility about 5%.

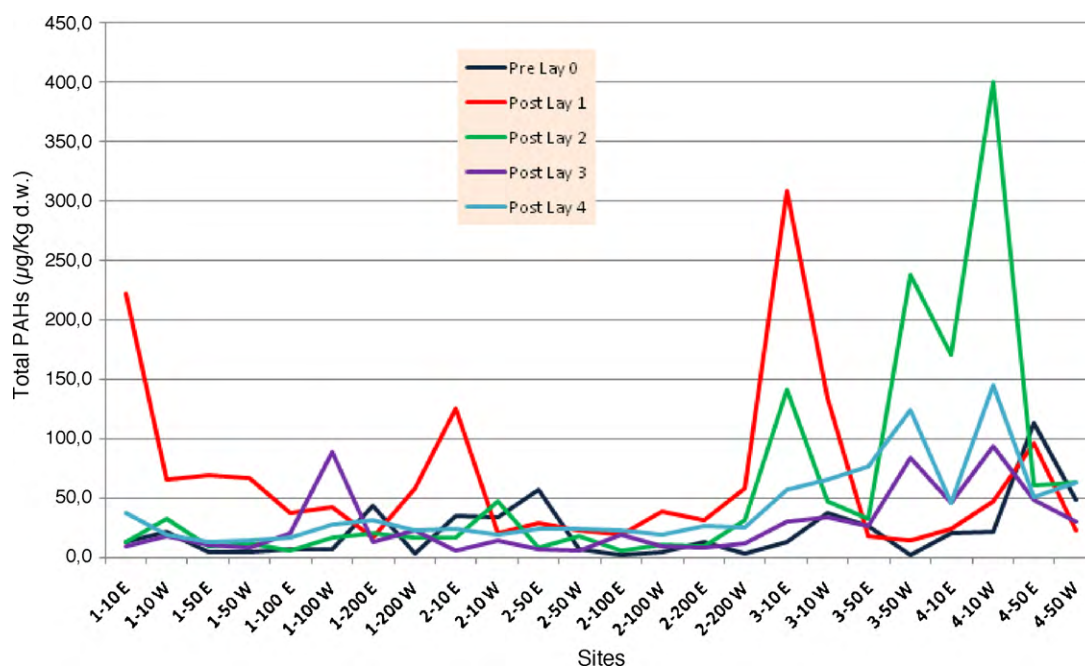


Fig. 2. Total PAHs ( $\mu\text{g}/\text{Kg d.w.}$ ) in the different sites and surveys.

### 2.7. Statistical methods

Principal component analysis (PCA) along two components was then carried out on data including 120 sampling stations as variables and 16 PAH compounds as objects. All data were block-normalised and weighted to average. XLStat software from Microsoft was used for PCA.

## 3. Results

The total PAHs contents varied considerably both between the different sites in the same survey and in the same site but in different surveys (Fig. 2). The wide range of PAHs concentrations (relative standard deviation ranged from 81 to 156%) found in the sediment samples, within the same survey, indicates heterogeneous levels of contamination in the investigated area. The heterogeneity of the levels found in the area can be interpreted on the basis of the spatial heterogeneity of the bottom conditions (organic matter content, etc). For example, binding of PAHs to humic matter influences their degradation in the soil.

The total concentrations (averages of the three analyses) for the 16 investigated compounds, expressed as the sum of the concentrations ( $\Sigma\text{PAHs}$ ) in the sediments of Gela coastal area, analyzed in the five surveys, ranged from 2.4  $\mu\text{g}/\text{Kg}$  to 434  $\mu\text{g}/\text{Kg}$  of dry weight (Fig. 2). The lowest concentration was measured in the site 2-100E during the pre-lay survey while the highest one (434  $\mu\text{g}/\text{Kg}$ ) was measured in the site 4-10W during the post-lay 2 monitoring survey, after the laying of the pipeline (Fig. 2).

From a comparison among the results of the pre-lay and the other surveys performed after the pipeline installation, a modification in the time of the concentrations of total PAHs can be observed. In the first and the second post lay surveys, highest PAHs concentrations were measured (mean values were respectively 67 and 68  $\mu\text{g}/\text{kg}$ ) compared to those in the pre-lay survey (24  $\mu\text{g}/\text{kg}$ ).

The water content determined in sediments sampled during the post lays 2 and 3 ranged from 22% to 44% and the organic matter content from 1.2% to 6%. The investigated marine area is mainly characterized, moving from coast off the shore, by sands, then muddy sands and muds (Fig. 5).

In the transect 1 (mean depth 9.1 m) muddy component in the sandy sediment ranges from 3 to 50%; in the transect 2 (mean depth 16.0 m) muddy component in the sandy sediment ranges from 3 to 30%. In the transect 3 (mean depth 24.5 m) sand component in the muddy sediment ranges from 14 to 38%; in the transect 4 (mean depth 32.5 m) sandy component ranges from 0 to 14%.

In the present paper, perylene was analyzed in all sediment samples with concentrations ranging from 0.022 to 34  $\mu\text{g}/\text{kg d.w.}$

## 4. Discussion

The increase of the total PAHs concentrations in the 1 and 2 post lay survey, could be attributed to the turbulence and mixing, due to the excavation of the seabed during the laying activities. During the other subsequent surveys, a progressive decrease of the total PAHs concentrations was observed to a level similar to that one recorded before the pipeline installation.

It's important to highlight that, except for two samples (1-10E and 3-10E both in the second survey), all total PAH concentrations in analyzed samples are lower than the national guideline limit: (0.2 mg/Kg) (G.U.R.I., D.M. 367/03, 2004) [37].

A comparison of PAHs in sediment along the Gela coastal area with published data [8,22,23,38–43] is difficult because of variances in the number and type of individual species determined in each study, the analyzed sediment fraction and the used analytical methods.

Anyway average levels of PAHs in Gela coastal area sediments were relatively low compared to the seas closer to other Sicilian areas, like the Stagnone coastal lagoon at Marsala (Italy) where the total concentration of PAHs ranged from 72 to 18381  $\mu\text{g}/\text{Kg}$  of dry matrix [23]. Recent studies from our group found mean levels of a sum of 19 PAHs throughout the Gulf and harbor of Milazzo (Italy) to be 5.4 to 7402  $\mu\text{g}/\text{Kg d.w.}$ , with an average value of 500  $\mu\text{g}/\text{Kg d.w}$  [44]. The comparison of the average total PAHs levels in the present study are low compared with the international studies worldwide [45].

According to Baumard et al. [46], PAHs contents can be described as low, moderate, high and very high when  $\Sigma\text{PAHs}$  concentrations are 0–100, 100–1000, 1000–5000 and > 5000  $\mu\text{g}/\text{Kg}$ , respectively.

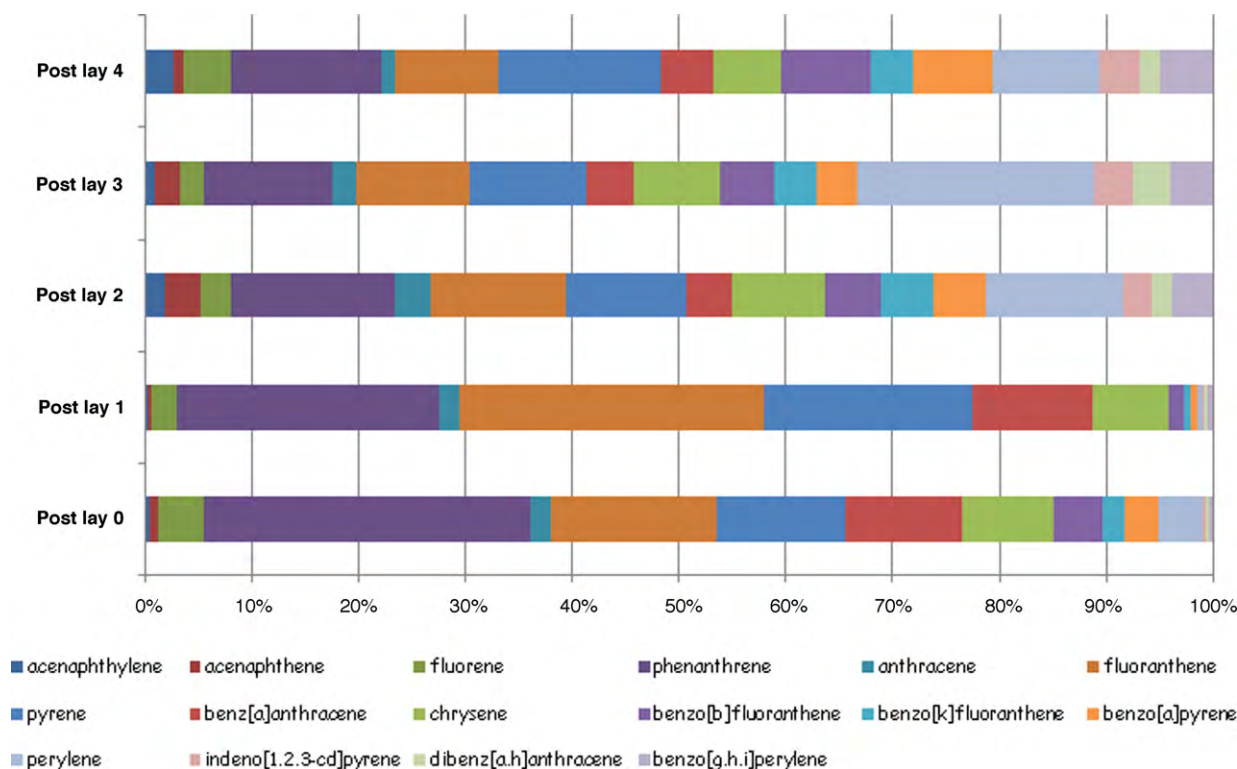


Fig. 3. Contributions of single compounds to total PAHs measured in the different surveys (mean of all the sites of a survey).

All stations except seven have PAHs concentrations  $<100 \mu\text{g}/\text{Kg}$  and are indicative of low contamination. Stations 1-10E, 2-10E, 3-10E and 3-10E (during the post-lay 1 survey) and 3-50W, 4-10E and 4-10E (during the post-lay 2) have PAHs concentrations of 222, 126, 308, 134, 238, 171 and 400 ( $\mu\text{g}/\text{Kg}$ ) respectively. On the basis of classification adapted by Baumard [46], the sediments from the Gela coastal area can be considered from low to moderate contamination with PAHs.

The PAHs concentrations found during this research are lower of those levels often identified as biologically unsafe [47] and even low- and medium-risk concentration ranges for PAHs (ERL =  $552 \mu\text{g}/\text{kg}$  and ERM =  $3160 \mu\text{g}/\text{Kg}$ , respectively) are higher compared to the average concentrations for Gela sediments.

Compositions and relative abundance of individual PAHs in most of the investigated sediments were more or less quite similar (Fig. 3). The 4 and 5-rings PAHs accounted for over 60% of the total PAHs concentrations in Gela sediments (Fig. 4). Also, during the post-lay survey 1, in almost all the stations, the percentage of 5 and 6 rings PAHs decreases. Four-ring aromatic hydrocarbons, such as phenanthrene, fluoranthene, pyrene, benz[a]anthracene and chrysene, were predominant among the analyzed PAHs except for some stations of pre-lay survey and post-lay survey 1 where the phenanthrene and fluoranthene were predominant.

Similarity of PAHs distribution suggests that the PAHs contamination in the Gela coastal area comes from similar sources.

According to the literature [48], two types of sediments are characterized by water content: sandy ( $\sim 20\%$  water) and muddy ( $\sim 40\%$  water). The latter are known to accumulate hydrophobic compounds to a much greater extent than sandy sediments and overall PAHs concentration is lower in sands than in mud [48].

For their hydrophobic character, the interactions of organic contaminants with sediments are determined by the organic content, the surface area and the nature of surface [49]. A nonpolar compound in an aquatic system is initially absorbed rapidly to the external surface of sediment particles, in particular to the organic matter that exists as external surface coating of clay minerals [50].

In fact, clay mineral in sediment represent a favourable site for the accumulation of organic matter [51]. This labile fraction is available for rapid desorption and is slowly converted to an unavailable fraction interacting with the most part of organic matter that resides inside the particles [52]. In this study, high concentrations of PAHs are present in sediments with high content of organic matter (e.g. stations 4-10, 4-50 during the surveys 2 and 3). This evidence has already been observed by a number of authors [53,54]. With the aim of identifying a relationship between the water or organic matter content and PAHs concentrations determined in the investigated sediments, a linear regression analysis was carried out. Linear correlations between PAHs total concentration and water and organic matter content (considering 20 stations) were found with  $r=0.79$  (mean of two surveys) for the water and with  $r=0.85$  (mean of two surveys) for the organic matter (Fig. 6). Four stations far from the coast, which showing strong deviations from the curves in both correlations, were not taken into account in the fits. Considering all the stations,  $r=0.55$  (mean of two surveys) for the water and  $r=0.53$  (mean of two surveys) for the organic matter were found. These results suggest that most of the PAHs identified in the samples originate from the same organic matter and that PAHs accumulate mostly on muddy sediments.

Separately considering the correlations at the different bathymetry, the values of  $r$  are very low ( $<0.1$ ), with the exception of eight stations located between the coast and the first bathymetry, during the survey 2, where values are between 0.87 and 0.90. When low regression coefficients for the organic matter vs. PAHs level relationship are found, as in this case, other elements probably play a major role in determining the level of contamination (e.g. proximity to sources, matrix characteristics). A mechanism can justify the PAHs concentration being low in muddy sediments but not in sandy sediments: the organic matter content can be closely correlated to the clay content of the sediment [55,56], so sediments with low organic matter content will be associated to low clay content. As a consequence, in sediments with a low organic matter, PAHs are not retained in labile organic fraction for a long time and the interac-

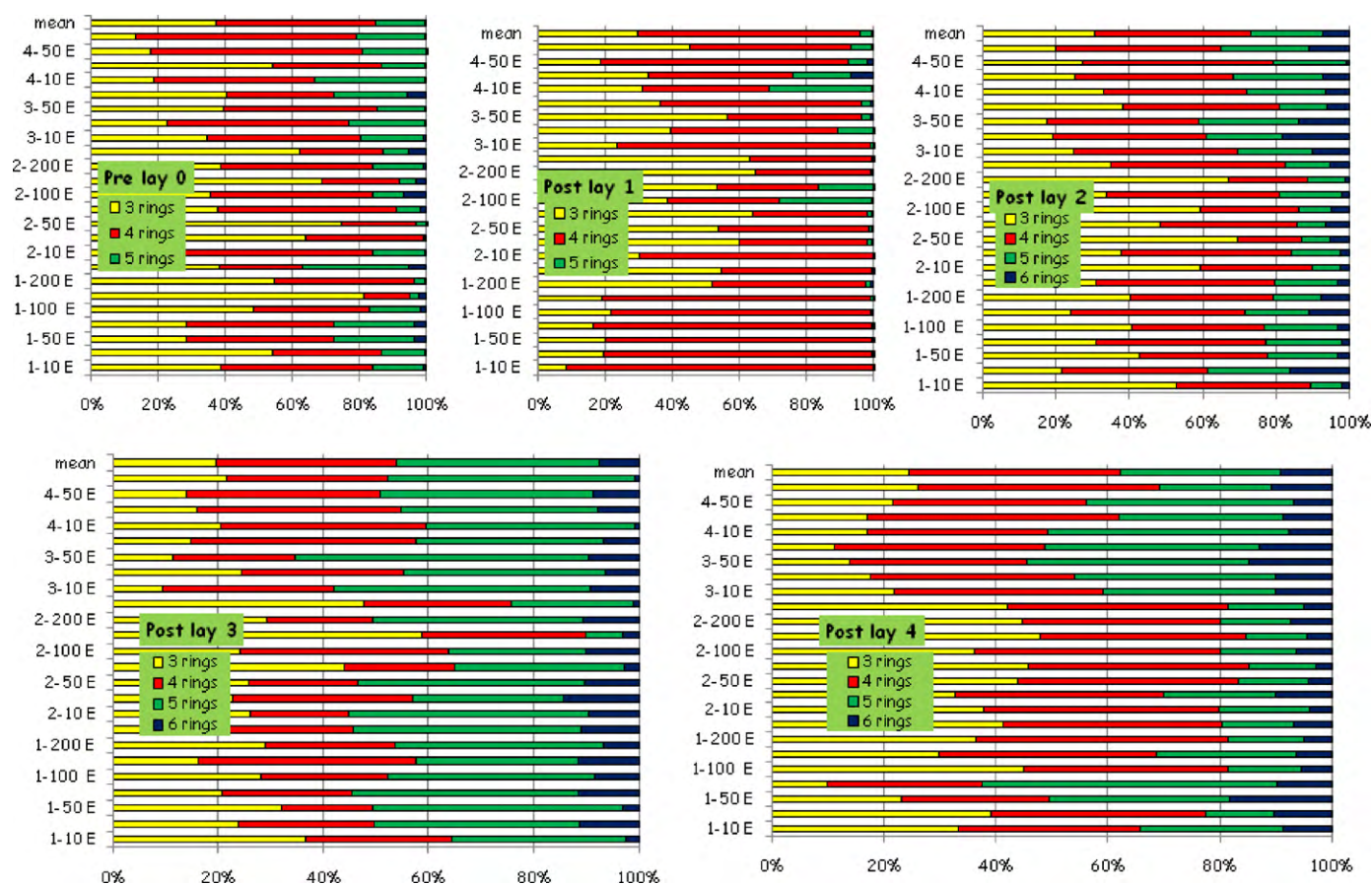


Fig. 4. Distribution of LMW PAH (3 ring PAHs) and HMW (4–6 ring PAHs).

tion with the inorganic matrix has greater importance. In sediment with low water and organic matter content, in fact, adsorption of non polar organics (as PAHs) is dominated by adsorption onto mineral surfaces [57]. Adsorption of non-ionic organic compounds by

the sediment mineral fraction is relatively unimportant in wet sediments, because of the strong dipole interaction between sediment minerals and water, which excludes neutral organic solutes from this portion of the sediment [58].

Regarding the origins of perylene, literature is discordant, some authors [35,59–61] argue that perylene can be produced from combustion of fossil fuels and biomass but the marked abundance precludes a pyrogenic origin; in fact, a perylene input of more than 10% indicates a diagenetic process. There is considerable evidence that it can be formed biologically under anaerobic conditions [22,34,62]. Several authors reported PAHs formation through plant and microbial metabolism [63] showing that wood from forest contains naphthalene, phenanthrene and perylene. Thiele and Brummer [62] reported that bio-formation of 3,4,5 and 6-rings PAHs was observed after incubation of fresh plant material and soil mixed with fresh plant material under reducing conditions. When only soil material was incubated, anaerobic biodegradation of three-ring was observed. Perylene quinones (pigments found in several insects, plants or fungi) are suspected to be degraded to perylene by anaerobic microbial metabolism [60,63]. Another theory postulates production via biosynthesis, independent of special precursors [63].

A perylene index, defined as concentration of perylene divided by the total of 5 rings PAHs isomers, has been proposed to distinguish biogenic perylene from pyrogenic perylene [34]. The perylene index greater than 0.1 frequently indicates the diagenetic (biogenic) inputs [34], whereas when it is less than 0.1, it indicates pyrogenic as origin of the compounds.

In the surveyed area, perylene concentrations remained almost stable in the stations close to the coast (up to the second bathymetry) where they began to increase.

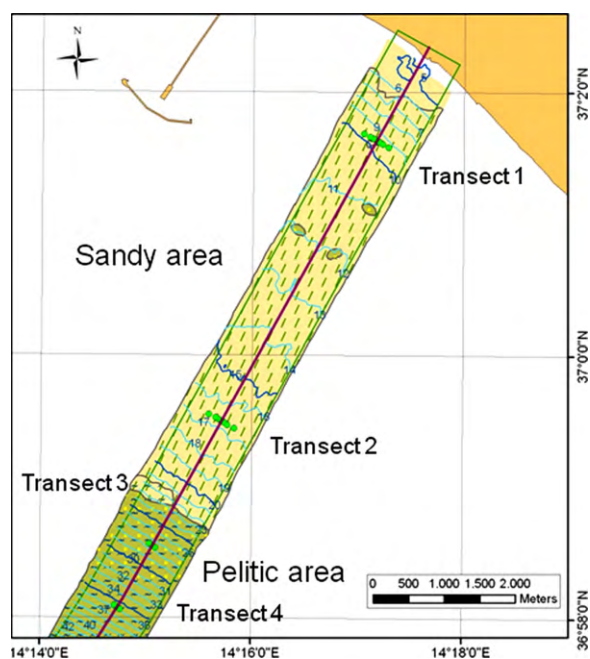


Fig. 5. Sedimentological pattern of investigated area.

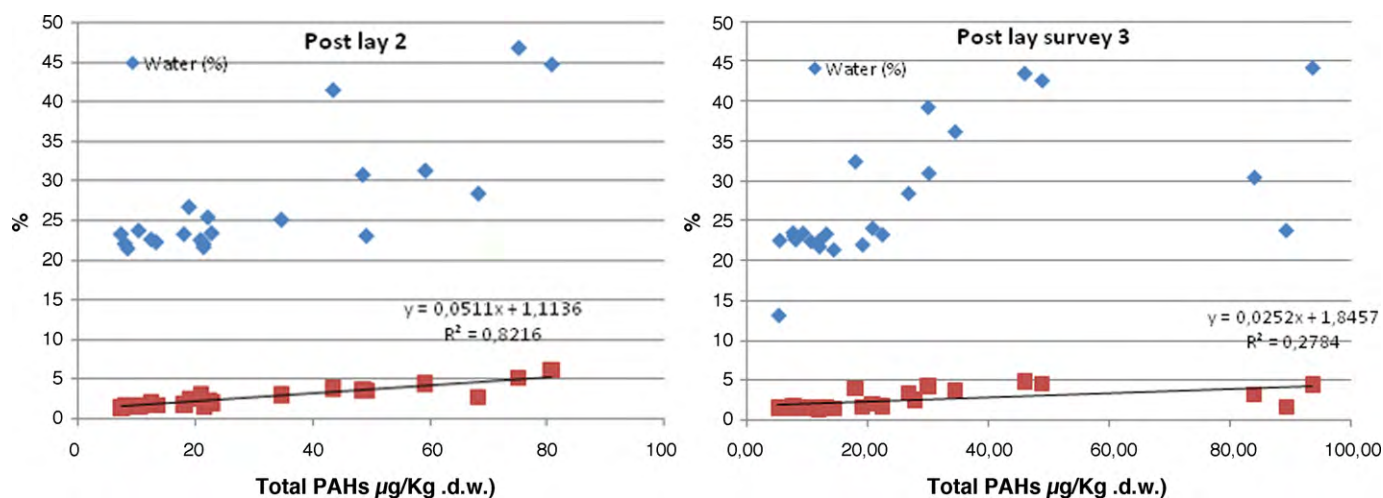


Fig. 6. Total PAHs concentration vs water and organic matter percentages in the sediments.

The relative indices were determined in the range of 0.03–0.84. Considering all the sites and the different surveys, the average values were in the range 0.2–1.6, determined in the post-lay survey 1 and during the post-lay survey 2 respectively. Values much greater than 0.1, suggesting perylene in these samples, originated mainly from its biogenic precursors.

The amount of perylene found in the near shore sediment was believed to originate mainly from terrestrial input. Perylene has been frequently associated with inputs from rivers and estuaries [34,53].

The presence of perylene in the analyzed sediments cannot be related to vehicular traffic because this analita occurs only in small concentrations in the atmospheric urban particulate; in fact the perylene index, in this case, is in the range of 0.02–0.04 (average value =  $0.027 \pm 0.07$ ) [21]. This conclusion is in agreement with the perylene behaviour which is not present or occurs only in small amount among the products of combustion processes, probably due to its thermal instability or reactivity [64].

High values were observed in stations far from the coast indicating diagenetic origin for the presence of perylene. This may be related to the high percentages of water (muddy) and organic matter and to anaerobic conditions of these sediments.

Some of the PAH analyzed in this context, especially the slightly volatile ones, are not regarded as carcinogenic. Within the remaining PAHs, substantial potency differences are in the size of several orders of magnitude. Because B[a]P is known to be the most carcinogenic compound, the carcinogenic potency of each collected sample was also determined in terms of its B[a]P equivalent concentration ( $B[a]P_{eq}$ ). To calculate the  $B[a]P_{eq}$  for each individual PAH species, the use of its toxic equivalent factor (TEF) is required for the given species relative to a B[a]P carcinogenic potency. In the literature, little data on TEFs are available only [65–67]. In our study the list of the TEFs by Nisbet and LaGoy [66] was adopted, as these have been demonstrated to be a better reflection of the actual state of knowledge on the toxic potency of each individual PAH specimen relative to B[a]P [68]. Concentrations of carcinogenic PAHs were calculated by:

$$TEQ = \sum(PAH_i * TEF_i)$$

where  $TEQ$  is the toxic equivalents of the reference compound;  $PAH_i$  is the concentration of PAH congener  $i$ ;  $TEF_i$  is the toxic equivalent factor for PAH congener  $i$ .

In sediment samples from Gela Coastal area, concentrations of  $B[a]P_{eq}$  ranged from 0.17 to 51  $\mu\text{g}/\text{Kg}$  d.w. Differences in the total carcinogenic PAHs concentrations (referred to as benzo[a]pyrene)

among the surveys were measured and the relative standard deviation is in the range 49–120%. Finally, the good linear correlation ( $r=0.92$ ) (Fig. 7) between carcinogenic PAHs and the total PAHs is worth noting.

Principal component analysis (PCA) was carried out to check the similarity of samples based on their composition. A 2-principal components analysis explained 80% of the variation. The loading plot reveals a separation between about 100 samples and about 15 samples far from the coast during the different surveys (4–50E, 3–50E, 3–50W, 2–200E, 1–200W, etc.). In particular, station 4–50W isolated from either of the two groups, possibly indicates a local different contamination of sediments. The main objects explaining the separation of the coastal stations from the rest are sandy sediments, while open sea stations are clearly defined by muddy sediments rich in organic matter.

#### 4.1. PAH sources determination

All analyzed sediment samples show elevated proportions of high molecular weight PAHs (4–6 rings) (HMW). The low molecular weight (3 rings) PAHs (LMW) are dominating only in 8 sites in pre-lay survey, 7 in the second, 4 in the third and fourth survey. The percentage of three, four, five and six ringed PAHs from different sites along the Gela coastal area are illustrated in Fig. 6. Low molecular weight PAHs compounds with 2–3 rings originate from petroleum products, incomplete combustion of fossil fuels and biomass at low to moderate temperature and natural digenesis, while high temperature procedures mainly generate high molecular weight PAHs components with 4 or more rings [69].

The ratio values of individual PAH species are often employed as diagnostic tools to identify the origin of PAHs in environmental matrices [70,71]. Diagnostic ratios should be used with care because inherent difficulty to in discriminating between different sources, moreover their values can be altered, due to reactivity of some PAH with atmospheric species.

The concentration ratios values of combustion (CPAHs) to the total PAHs ( $Fl + Py + B[a]An + Chry + B[e]Py + BFs + B[a]Py + B[ghi]Pe + IPy / \sum PAH$ ) were almost constant ( $0.56 \pm 0.036$ ) during all the monitoring surveys. The above values are in accordance to those reported for combustion sources and to those produced in small cities and remote locations of Macedonia (0.46–0.59) [72].

Although several constraints exist, molecular ratios of some marker PAHs have been used to identify sources of PAHs in the environment. Ratios of specific individual PAHs are characteristic



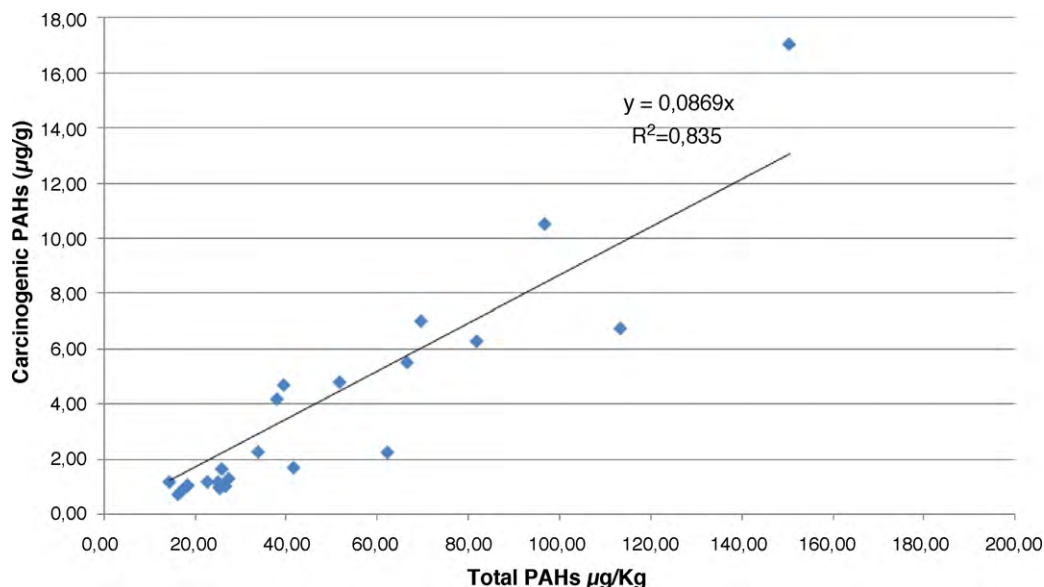


Fig. 7. Linear regression curve of total PAHs vs carcinogenic PAHs concentrations.

of different sources [34,73,74]. The results of diagnostic ratios used in this study are shown in Fig. 8.

An/(An+Ph) ratio lower than 0.1 indicates a petrogenic source while a ratio higher than 0.1 can be attributed to a combustion source [64]. The average of An/(An+Ph) ratios, considering all the sites, is greatly variable during the different surveys. The highest values (>0.1) of An/(An+Ph) ratios were found in sediments sampled in the sites far from the coast and deep.

The average ratios were in the range 0.054–0.14; the minimum mean value (0.054) was measured in the pre lay survey and the maximum in the post lay survey 3 (0.14). Based on the 0.10 transition [26] An/(An+Ph) ratios suggest mixed sources in the investigated area.

A Fl/(Fl+Py) ratio <0.4 is generally characteristic of petrogenic sources (oil, diesel, coal), between 0.4 and 0.5 it indicates liquid

fossil fuel (crude oil and vehicle) combustion, whereas a ratio over 0.5 is generally found in kerosene, grass, coal and wood combustion samples and creosote [26,64]. For gasoline, diesel, fuel oil, crude oil combustions and emissions from cars and diesel trucks Fl/(Fl+Py) ratio is less than 0.5 [26].

Considering all the surveys, for the samples collected along the Gela coastal area, mean ratios Fl/(Fl+Py) ranged from 0.50 to 0.58. In agreement to the values of ratios Fl/(Fl+Py) reported in literature [26] PAHs in the investigated area can be considered of pyrolytic origin.

Considering all the surveys, the mean values of the BaA/(BaA+Chr) of different sites ranged from 0.07 to 0.49 with an average value of 0.35. The data of literature [26] suggest that BaA/(BaA+Chr) ratios from 0.20 to 0.35 it indicates either petroleum or combustion and >0.35 imply combustion. The analytical data in our study indicate that PAHs found in the main part

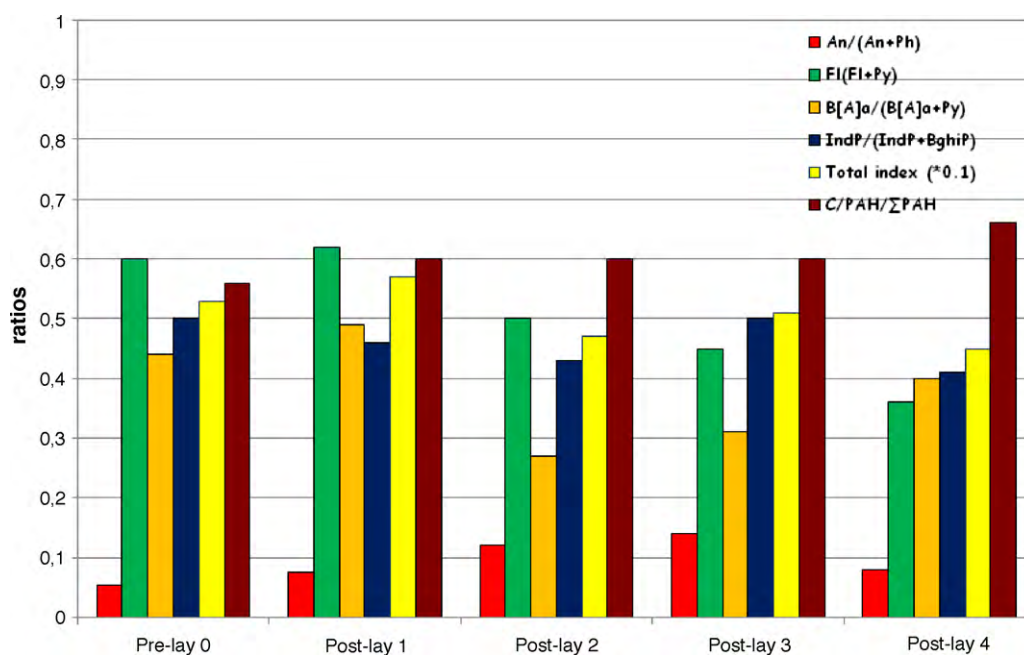


Fig. 8. Diagnostic ratios.

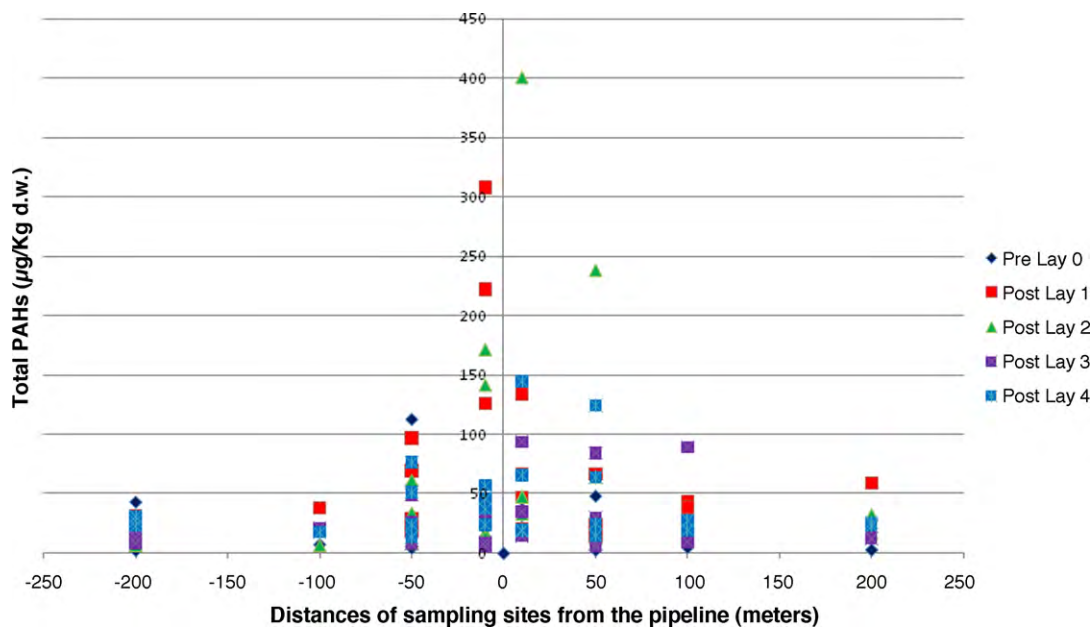


Fig. 9. Total PAHs at East and at West of pipeline.

of the stations seem to be of pyrolytic origin as a major source of PAHs.

According to the data of literature [26], IP/(IP + BghiP) ratios of 0.20 likely imply petroleum, between 0.20 and 0.50 liquid fossil fuel (vehicle and crude oil) combustion, and ratios > 0.50 imply grass, wood and coal combustion. In our case, considering all the surveys, the mean ratios ranged from 0.41 to 0.50. The analytical data indicate that PAHs found in the most of stations seem to be of pyrolytic origin.

In some cases, the values of the four ratios are not always in agreement, and considering that, the sources of PAHs in a matrix can generally result different and occasional, a total index has been calculated [13] as the sum of the single index (before discussed) respectively normalized for the limit value (low temperature sources-high temperature sources) reported in literature [26].

PAHs are prevalently originated by high temperature processes (combustion) when total index is > 4 while lower values indicate prevalently low temperature sources (petroleum product). Considering all the surveys, the results (Fig. 8) obtained from the total index, confirm that all the PAHs identified in the sediment samples of the different sites originate, mainly, from combustion processes.

The ratio of BaA/Chr could be used to evaluate the distance of the source of PAHs from the studied area. The lower ratio of BaA/Chr implied longer distance of transport, while the higher ratio would suggest that those PAHs might be originated mostly from the emission of the local sources [75,76]. Considering all the surveys, the mean values of BaA/Chr were in the range 0.8–2.2, indicating that most PAHs in sediments of Gela Coastal area might be transported from very close sources. Fig. 9

#### 4.2. Conclusions

Our main remarks are as follows:

(a) The results reported in our work represent the first quantitative investigations of PAHs in superficial sediments of the Gela coastal area. Levels of PAHs found in this paper will also serve as a baseline for the future excavations or when other marine works will begin in the investigated area. It is known

that in environmental damage assessments it is very useful to have informations about sources of contaminants present in the affected area before activities or accidents take place.

- (b) The greater presence of PAHs with high molecular weights in most samples, the isomeric ratios and the total index values used as PAHs distribution indexes demonstrate that most samples owe their PAHs a predominant single origin, i.e. anthropogenic combustion or pyrolytic processes, while a negligible quantity of PAHs may derive from biogenic sources since all the sediments contain perylene traces.
- (c) A meaningful increase on total PAHs content can be noticed for the post-lay survey 1 compared to the pre lay survey 0. This evidence is in accordance with the density variation of the marine vegetation in the investigated area: the pre lay survey 0 shows a diffuse presence of the *Cymodocea nodosa*, a condition not confirmed by the first lay survey, where no more meadows appear [36], probably stifled by suspended sediment caused by pipe burying operation. However, in the subsequent post lay surveys, a gradual decrease of total PAHs concentrations was observed together with a resumption of the vegetable species, in a clear stage of increase.

The monitoring plan addressed to control the evolution of PAH concentrations of the shore approach in Gela, due to the pipeline installation, has allowed us to underline the reversible character of the impact on the marine environment and in particular on the surface sediments.

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