

Research on polycyclic aromatic hydrocarbon pollution in sediments and waters of northern Lebanon: rivers, transition zones, and port sites

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Abstract: Contamination of the marine environment is associated with continental activities, marine activities and accidental spills. Providing answers to the origin of the contamination of the aquatic environment by PAHs is an objective of the present work. The originality of this work is to study pollutants in two types of matrix (water and sediments) during 2 seasons (dry and wet) for an environmental monitoring of 6 years. This study provides a more complete overview of the state of contamination in three coastal rivers, their transition zones and harbors in the Eastern Mediterranean following the Jiyeh oil spill in 2006.

Contaminants concentrations were expressed as the sum of the 16 PAHs classified as priority substances by the United States Environmental Protection Agency (US-EPA). Overall, contamination was noted for all the analyzed sites. Oil spill seemed to be one of the main sources of pollution in the area, as the highest levels of PAH ($> 9,000 \text{ ng.g}^{-1} \text{ p.s}$ and $> 8,000 \text{ ng.L}^{-1}$) were reported in the coastal environment of the three rivers and harbors.

High levels of PAHs were also observed in the transitional zones of rivers, revealing the importance of terrestrial inputs (untreated wastewater discharge, leachate, solid wastes, etc.).

Comparing the PAHs concentrations measured in the sediments of the sites analyzed with the empirical sediment quality criteria "SQG" for the support of the general assessment of sediment toxicity, we can notice that some individual PAH and their sum can present a significant ecotoxicological risk to aquatic organisms. Further research through monitoring campaigns and toxicity tests is encouraged, as the exposure of the resident aquatic organisms and human population to these chemicals might be expected to increase over the years.

Key words: polycyclic aromatic hydrocarbons (PAHs); toxicity; sediment; water; rivers; ports

1 Introduction

The Lebanese coast was hit by a massive fuel oil spill from 13 to 15 July 2006 following the bombing of the tanks at the Jiyeh thermal power plant, located along the coast 30 km south of Beirut, Lebanon. A spill of around 15,000 tonnes of heavy fuel oil (IFP-number 6 fuel 4) occurred, with a fire that burnt around 5,500 tonnes of this fuel oil over more than three weeks, releasing a haze of dioxins and harmful chemicals into the atmosphere (MOE, 2006). The fuel oil contained in the tanks was a heavy type with a high viscosity, high density ($950\text{-}1,030 \text{ kg.m}^{-3}$), a tendency to separate into tar balls and sink to the bottom, and a low volatility that limited evaporation. Its viscous nature has led to its prolonged persistence in the marine environment.

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The plume from the southern coast extends from Jiyeh south of Beirut along the Lebanese coast to the Syrian border. Less than 10% of the oil spilled off the east coast of the Mediterranean has been recovered (MOE, 2006). Khalaf et al (2006) measured concentrations of the 16 US-EPA PAHs in the sediments at Jiyeh of $1,416 \mu\text{g}\cdot\text{g}^{-1}$ dw; these values were higher than those found in the Erika and Prestige oil spills ($949 \mu\text{g}\cdot\text{g}^{-1}$ on the French coast and $902 \mu\text{g}\cdot\text{g}^{-1}$ on the Spanish coast respectively).

PAHs are emitted into the environment via natural phenomena and via anthropogenic activities, the latter having been estimated as the main sources (Assunção et al., 2017; Baek et al., 1991; Eisler, 1987). PAHs come from two main sources: pyrolytic and petrogenic.

Sources can be identified by the distribution of all parent and alkylated PAHs or "molecular profile", by the use of PAHs that are markers of a specific origin (e.g. the case of perylene mainly from early diagenesis) or by the use of concentration ratios between compounds from different sources. Phenanthrene/anthracene and benzo(a)anthracene/chrysene concentration ratios can thus be used as qualitative indices to discriminate between sources of contamination of pyrolytic and petrogenic origin in an environmental matrix (Budzinski et al., 1997; Baumard et al., 1998 a, b; Raoux, 1991; Wang et al., 1999; Yunker et al., 2002). Many other indices have been described in the literature (Budzinski et al., 1997 ; Maciel et al., 2015 ; Yunker et al., 2002). The reliability of these indices is based on the use of pairs of isomers, i.e. compounds with the same molecular weight and the least differences in their physicochemical characteristics and fate in the environment. The robustness of an index is also based on the extent of the difference between the thermodynamic stabilities of the compounds. Yunker et al (2002) determined that isomers with molecular weights of 276 [including the Indeno (1,2,3 cd) pyrene and Benzo (g,h,i) perylene pair] and 202 (Fluoranthene/Pyrene) show the greatest differences in the energy of formation required and may be good indicators of the sources of contamination of the matrices analyzed in this work.

PAHs are known to be ubiquitous contaminants in the marine environment (Assunção et al., 2017; Tolun et al., 2006), originating from continental activities and activities carried out in this environment. The literature shows that the most contaminated coastal areas are those under urban or industrial influence, and those subject to heavy maritime traffic such as ports. Natural sites and those located offshore are less affected. In the Mediterranean, total PAH concentrations are comparable to those in other non-Mediterranean sites (Hellou et al., 2005; Zeng et al., 2002). However, PAH levels in sediments are generally higher than that in the aqueous phase (Karacik et al., 2009; Tolun et al., 2006). As expected, sediments collected from urbanized sites and harbour sites show the highest levels of these contaminants (Astrahan et al., 2017; Baumard et al., 1998 a; Bihari et al., 2006; Eljarrat et al., 2001; El Nemr et al., 2007; Karacik et al., 2009, Manneh et al., 2016). In marine sediments, wide ranges of PAH concentrations have been observed along the Mediterranean coast, with concentrations that can be up to 100,000 times higher than that in water. In Lebanon, Merhaby et al (2015) measured total PAH concentrations in the sediments of the commercial port of Tripoli ranging from 243 to $2,965 \text{ ng}\cdot\text{g}^{-1}$ p.s.; these concentrations were significantly higher than those measured by Manneh et al (2016) in the surface sediments of other ports in Lebanon. The lowest concentrations were found in Tyre ($1.22 \text{ ng}\cdot\text{g}^{-1}$ dw) and the highest in Dora and Jounieh ($732 \text{ ng}\cdot\text{g}^{-1}$ dw). In Spain, total PAH concentrations in sediments along the Catalan coast varied from 13.4 to $16,700 \text{ ng}\cdot\text{g}^{-1}$ dw. (Eljarrat et al., 2001), while in the waters of the port of Masnou, these concentrations ranged from 226 to $331 \text{ ng}\cdot\text{L}^{-1}$ (Perez et al., 2003). Significantly lower concentrations have been observed in lagoons (Trabelsi et al., 2005) and in sediments taken from the open sea (Gogou et al., 2000; Hatzianestis et al., 1998). In addition, PAHs are considered persistent organic pollutants due to their stable chemical structure and inherent resistance to biotic and abiotic decomposition (Baniemam et al., 2017).

In addition, there are few studies on these organic pollutants in the Eastern Mediterranean, an area characterized by significant demographic growth and discharges of untreated effluent into aquatic ecosystems.

The main objective of this study is to assess the impact of human activities and the vulnerability of sediments in the Eastern Mediterranean region in the absence of wastewater treatment plants (WWTPs). Univariate and multivariate statistical techniques were applied in order to obtain environmental data on the spatial and temporal trends of these pollutants and to distinguish firstly between the different sources of PAH pollution (pyrolytic, petrogenic and mixed) and secondly by the types of input (marine and/or continental inputs). They are used to exploit correlations between the different sampling sites, seasons and contaminant origins. Finally, the sediment data were compared with empirical sediment quality criteria (SQG) for a general assessment of the toxicity of coastal sediments.

2 Materials and methods

2.1 Sampling strategy

As the aim of this work is to study the transition zones between fresh and salt water, the sampling points are located near the river mouth, 6.5 km for the El-Kébir River (EK), 3.1 km for the El-Bared River (EB) and 9.5 km for the Abou Ali River (AA).

For the city of El-Mina (M), 6 sectors, extending from the commercial port in the north of the city in the coastal environment of the Abu Ali River to the Olympic stadium, approximately 10 km from the commercial port in the south of the city, were selected along its coast in order to present the various types of polluting activities that exist along the coast. These sites include: the commercial port of Tripoli, the Tripoli landfill site, the fishing port of El-Mina, and the sewage discharge sites in the city of El-Mina (Figure 1). The sites were selected on the basis of their location in relation to built-up areas, sources of pollution and accessibility.

A six-year sampling programme (2010-2016) was launched and three sampling campaigns were carried out per year; in August, October (dry period) and January (wet period), each covering 37 points. These 37 points include: 31 points along the sectors selected for the three rivers (EK, EB and AA) and 6 points along the sectors selected for the town of El-Mina (M). Due to the size of the study area, surface water and surface sediment samples were collected over a period of 2 to 4 days.

Water: For each of the 37 sampling sites, several samples of surface water (0-50 cm) were collected in 1-litre amber glass bottles before being homogenized. The environmental samples taken depended on the depth and geographical location of the sites. For each sampling point, three 1-litre bottles were immersed (10-50 cm) over a width of 1 to 2 m, and the samples were homogenized to obtain a composite sample (3 litres) per point.

Sediment: For each of the 37 sampling sites, 500 g - 1,000 g of sediment (0-20 cm deep) was collected, in accordance with EPA (2001) methods. Several samples were taken at each site, covering an area of 1 to 2 m². Depending on the depth and texture of the sediment, several techniques were adopted. A metal spatula was used for sites with little sediment. A stainless steel grab was used at sites along both banks of each of the three rivers, as well as along the coast of the town of ElMina, which were accessible on foot. A Van Veen grab was used for muddy or sandy sediments where the depth was sufficient to close the grab. This type of grab was used to collect sediments in transition zones and sediments from the coastal environment of the 3 rivers, as well as sediments from the commercial port and the fishing port.

Water salinity and dissolved oxygen (DO) were measured at the sampling sites. These measurements enabled three physically different zones to be determined for each river: coastal (C), transitional (T) and upstream (A), with salinities of 32 g.L⁻¹, 0.26 g.L⁻¹ and 0.08 g.L⁻¹, respectively. Thus, for each river 3 points (c1, c2 and c3) represent the coastal environment (C) of the river discharge, 3 points (I, II and III) represent the transition zone (T), and 5 points (IV, V, VI, VII

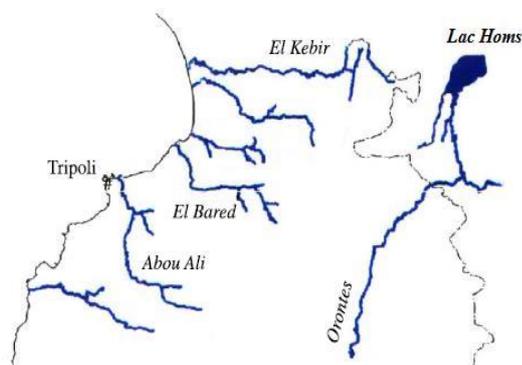
and VIII) represent the zone upstream of the mouth (A) (with the exception of El-Bared where 3 sites represent this zone). The six sectors along the El-Mina coast include: the commercial port (Portcom), the fishing port (Portpe), and the four sewage discharge sectors (MIII, MIV, MV and MVI) (Figure 1).

El Bared River

Site #	D (km) From mouth	Zone	Description
EB I	0		Transition Zone
EB II	0	T	Transition Zone
EB III	0		Transition Zone
EB IV	0.1		At the end of the river
EB V	1.1		Palestinian Camp
EB VI	3.1	A	Urbanized areas Agricultural areas
EB c1			Coast (Palestinian Camp)
EB c2	Emission Zone	C	Coast (Mouth)
EB c3			Coast (South)

Kebir River

Site #	D (km) From mouth	Zone	Description
EK I	0		
EK II	0	T	Transition Zone
EK III	0		
EK IV	0.2		At the end of the river
EK V	1.0		Bedouin population
EK VI	1.5	A	Urbanized areas
EK VII	3.5		Agricultural areas
EK VIII	6.5		Agricultural areas
EK c1			Coast (Syrian side)
EK c2	Emission Zone	C	Coast (Mouth)
EK c3			Coast (Lebanese side)



El Mina City Coast

Site #	D (km) Commercial Port	Description
Portcom	0	Port commercial
Portpe	1.8	Fishing port
M III	3.6	
M IV	5.4	Sewer outfalls
M V	8.5	
M VI	10.5	

Abu Ali River

Site #	D (km) From mouth	Zone	Description
AA I	0		Transition Zone (STEP)
AA II	0	T	Transition Zone (Mouth)
AA III	0		Transition Zone (Emissions)
AA IV	0.3		At the end of the river
AA V	1.4		Leachate leakage - discharge
AA VI	1.8	A	Tripoli entrance
AA VII	4.9		Urban and agricultural areas
AA VIII	9.5		
AA c1			Coast (STEP)
AA c2	Emission Zone	C	Coast (Mouth)
AA c3			Coast (Emissions)

Figure 1. The general conditions met by each sampling point on the three rivers and coast of El Mina city

2.2 Reagents and materials

2.2.1 Select substance

Sixteen polycyclic aromatic hydrocarbons (PAH mixtures) concentrated to $100\text{ng}\cdot\text{ul}^{-1}$ in cyclohexane were purchased from Dr. Ehrenstorfer, GmbH (Germany).

2.2.2 Internal standards

Internal standards are used to calculate extraction rates and control all operations from extraction to GC-MS quantification. Chrysene-D12 (purity 99.9%) is provided by Sigma Aldrich (Steinheim, Germany) as an internal extraction standard for liquid and solid samples. PCB30 (CDN isotope, purity 96.5%) was provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany) and used as an internal standard for GC-MS injection to control injection volume.

2.2.3 Solvents

All solvents used for analysis and extraction are pesticide grade, and the solvent used for gas chromatography is ultra pure (99.9%).

Standard sediment reference material (3 ± 0.5 g) was used for the validation of PAH extraction and quantification methods (Freshwater harbour sediment, BCR 535 - BCR)®).

2.3 Extraction and chromatographic analysis methods

2.3.1 Solid phase extraction (SPE) of water

Water extraction (1 L) was carried out after filtration on GF/F filters (Whatmann®) of 150 mm diameter per SPE. LC-18 type SPE cartridges weighing 1 g (Supelclean TM LC-18, 6 mL, 1 g, Supelco, Bellefonte, USA) are used. After elution, the extracts were filtered over anhydrous sodium sulfate and glass wool contained in 5 ml Omnifix® syringes supplied by B/Braun, then evaporated dry under a stream of nitrogen (< 2 Psi) and taken up, at a rate of 3 fractions, in 1,000 μ L of heptane containing PCB 30 to 0.1 $\text{mg}\cdot\text{L}^{-1}$ as an internal injection standard. All the steps were carried out on a visiprep TM DL (Supelco) equipped with 12 liners for the extraction of aqueous samples. The calibration range is set between 1 and 200 $\mu\text{g}\cdot\text{L}^{-1}$ by successive dilutions in cascade, using heptane.

2.3.2 Microwave assisted extraction (MAE) of sediment

The microwave-assisted extraction method for sediment extraction is adapted from the validation method described by David et al. (2009), Kinani et al. (2010), and Parera et al. (2004) for extracting organic pollutants from freeze-dried and ground sediments (5 ± 0.5 g/extraction fraction < 2 mm). This technology involves extracting organic pollutants from a solid matrix using one or more organic solvents placed under high temperature and pressure. A Multiwave 3000 microwave oven (Anton Paar) equipped with 8 liners is used for solid sample extraction processes. It is fitted with a patented M50 pressure/temperature sensor (US Patent 5601745).

In order to avoid damaging the analytical column during GC-MS chemical analysis, a procedure was employed to remove sulfides present in sediment extracts used for chromatographic analysis (EPA-3 660B for sulfide cleaning). The subsequently obtained extract is filtered on a Suppor filter® 200 (Par, Mexico), diameter 47 mm, pore size 0.2 μ m, filled with approximately 10 g anhydrous sodium sulfate, then evaporated to dryness using a rotary evaporator in a 35°C water bath. Dissolve the dry extract in 1,000 μ l of heptane, which contains the internal injection standard (PCB 30) for chemical analysis three times.

2.3.3 Analysis of PAHs

Analyses were performed using a Ultra Trace 3000 GC (Thermal) coupled with Polaris Q mass spectrometer (thermal) with a 70 eV electron shock ionization chamber. Chromatographic separation was performed with an SGE-BPX5 capillary column of 30 m \times 0.25 μ m (internal diameter) (stationary phase: 5% phenyl polysilphenylene-siloxane). The maximum time to fill the trap is 25 ms. The injections were made using an automatic AI/AS 3000 self-sampling injector. GC vials with and without a 2.5 ml Fisher brand insert were used to inject extracts into GC. 1 μ L of the solution to be analyzed is injected into a 250°C glass wool injector in split/splitless mode, splitless mode for 1 minute before replacing into split at a

flow of 50 mL.min⁻¹. The data were interpreted using the Xcalibur software provided by Thermo.

For 16 types of polycyclic aromatic hydrocarbons, the chromatographic method is as follows: the initial temperature is 60 °C and kept constant for 1 minute. Then, four consecutive heating slopes are performed: the first rises to 140°C, increasing by 13°C. min⁻¹; the second rises to 180°C, increasing by 8°C. min⁻¹; the third rises to 220°C, increasing by 5°C. min⁻¹; and the fourth rises to 300°C, increasing by 3°C. min⁻¹. The final temperature was kept constant for 10 minutes. The program lasted for approximately 50 minutes in total. Under these chromatographic conditions, 16 polycyclic aromatic hydrocarbons were well separated (Figure 2).

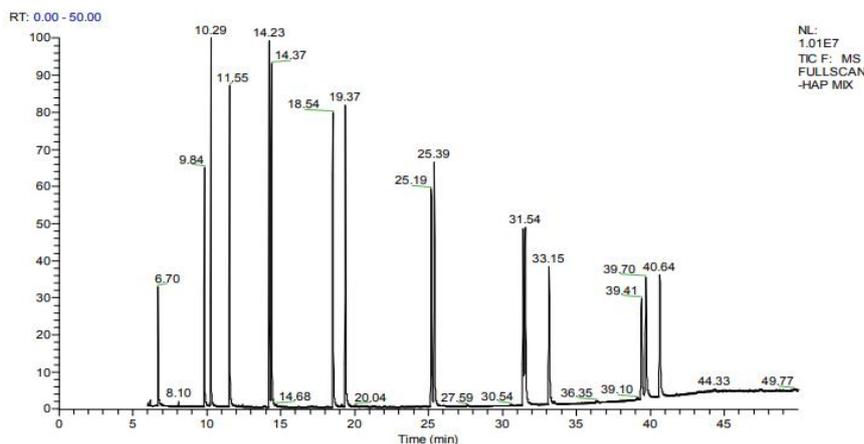


Figure 2. Full scan chromatograms of 16 preferred polycyclic aromatic hydrocarbons concentrated to 1mg.L⁻¹

Each of the 16 PAHs is identified according to its retention time in addition to one or two quantification ions. A 3rd quantification ion is identified to increase the specificity of detection. Quantification is based on a comparison of the peak height with that of the relative standard.

2.3.4 Quality control: validation of analytical methods

All glassware was thoroughly cleaned with acetone and dichloromethane and dried. Reagent blanks were analyzed regularly and all data presented in this study were corrected with the blank values.

The statistical study of the results showed that the calibration range of 16 polycyclic aromatic hydrocarbons was consistent with the 1 µg linear model. L⁻¹ to 200 µg. Water with a correlation coefficient greater than 0.99 is considered L⁻¹, while sediment has a dry weight (dw) ranging from 1 ng.g⁻¹ to 250 ng.g⁻¹.

During the validation phase of this method, BCR certified sediments were extracted: intra day repeatability n=3, inter day repeatability n=9. River water was extracted to calculate extraction yields - water. The average extraction yields (n = 3) and their associated standard deviations obtained were 91 ± 4% for certified sediments and 98 ± 9% for water.

The expected concentration deviations of different substances analyzed in water and sediment are -11% to +10% and -8% to +15%, respectively. For all substances analyzed in water and sediment, the coefficients of variation for the three concentration levels are less than 12% and 13%, respectively.

To calculate the quantitative limits in different matrices, the average absorption volume of each extract from water and sediment was 1,000 µL, which is equivalent to an average of 1 liter of water and 5.50 grams of sediment per milliliter. The obtained quantitative limits (95 ng.L⁻¹ for water and 1.7 ng.g⁻¹ for sediment) allow for the analysis of the required pollutants in different types of environmental matrices (surface water, seawater, and sediment).

2.3.5 Statistical studies

SPSS (statistical package for social sciences) version 23.0 was used for the statistical analysis.

For the validation of extraction and quantitative methods: To ensure the linearity of the methods, ANOVA was used to test the homogeneity of variance using SPSS ®. The original standard deviation of slope and vertical axis is calculated with a 95% confidence interval.

For the analysis and interpretation of the results: Normality and equal variance tests were performed before the ANOVA. Analysis of variance (ANOVA) was followed by multiple comparison tests such as Tukey's HSD test and Fisher's LSD test, respectively, to assemble the sites according to their salinity into homogeneous subsets (zones of C, T and A), and to determine which zone and which sampling period differed when significant differences between the means were detected via ANOVA or simply when the variances were not equal.

3 Results and discussion

3.1 Polycyclic aromatic hydrocarbon pollution level: spatiotemporal and spatial variations

3.1.1 Spatial changes

Figure 3 shows the total concentration of polycyclic aromatic hydrocarbons (PAHs) measured in sediments sampled in upstream (A), transition zone (T), and coastal area (C) (coastal environment of three rivers) and six regions (Portcom, Portpe, MIII, MIV, MV, MVI) between 2010 and 2016. These regions display specific inputs along the El Mina coastline (ports, sewage discharge points).

The concentration of polycyclic aromatic hydrocarbons is expressed as the sum of 16 priority polycyclic aromatic hydrocarbons recommended by the United States Environmental Protection Agency. Overall pollution was observed at all analysis sites and in all three sampling activities. The concentration levels of sediment and water samples in the coastal environment of the three rivers are 958 to 1,800 ng.g⁻¹ dw and 900 to 8,000 ng.L⁻¹, respectively. These concentrations are higher than those in the transition zones of three rivers (254 to 463 ng. g⁻¹ dw, 115 to 600 ng. L⁻¹) and upstream (112 to 250 ng. g⁻¹ dw, <LD to 3,500 ng.L⁻¹). The maximum concentration of polycyclic aromatic hydrocarbons (PAHs) was measured in sediments and port waters (4,021 to 9,065 ng.g⁻¹ dw, 5,800 to 8,000 ng.L⁻¹).

Among these three rivers, the most polluted one is the sediment collected from the Abu Ali River, while the pollution levels of the Kebir River and the Bared River are similar. The coastal sewage leakage sites (MIII, MIV, MV, and MVI) in El Mina city and the coastal sediments in zone C of three rivers show the same total pollution level of polycyclic aromatic hydrocarbons, about several thousand ng.g⁻¹ dw. These two ports have concentrated a large amount of continuous professional activities throughout the year, and the pollution level measured in this study is the highest. Almost all sediments collected from the upstream of the three rivers are free of polycyclic aromatic hydrocarbon pollution, with concentrations below several hundred ng.g⁻¹. The concentration of sediment in the transition zones is between site C and A.

Coastal sediments are mainly composed of medium sand (125-500 μ m), with an average concentration higher than that of transition zones and upstream samples, and finer particle size (<63 μ m). However, these observations emphasize the specificity of some sandy (coastal) sediments, which are heavily polluted due to the input type (floating oil).

These data are collected from three sampling activities each year, covering both dry and rainy seasons. Overall, they can emphasize the heterogeneity of polycyclic aromatic hydrocarbon concentrations, which is related to significant spatial variability in the absence of any temporal trend. The sediment pollution level is the highest in coastal areas; the spatial variability of its concentration is almost zero (AA-C, EB-C, EK-C, MIII, MIV, MV, and MVI).

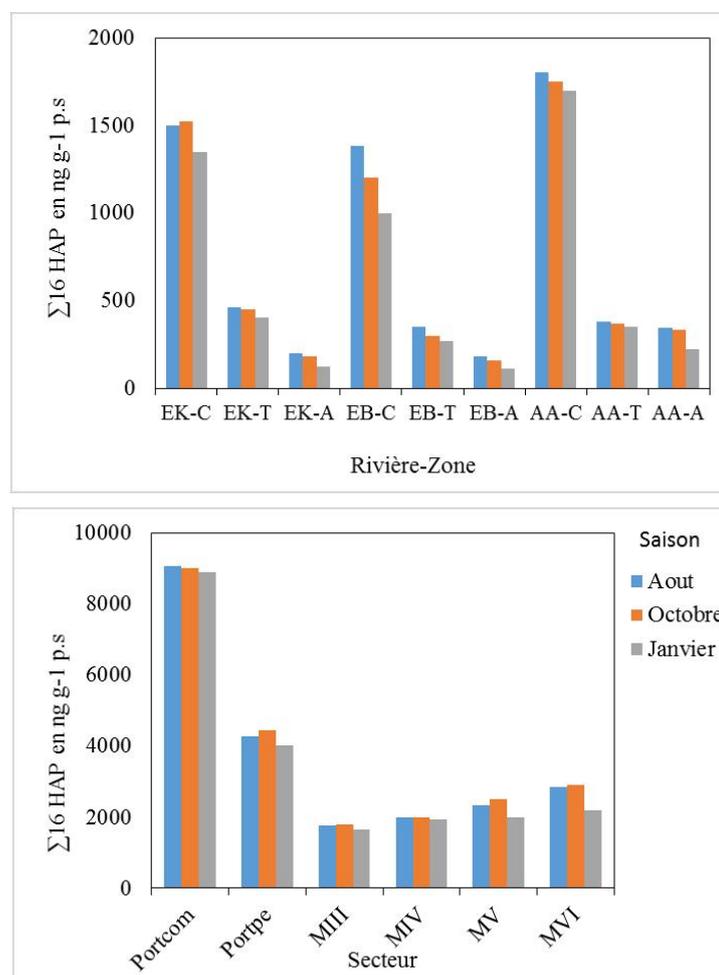


Figure 3. The average ng.g^{-1} concentration of total polycyclic aromatic hydrocarbons (Σ 16 PAHs) by dry weight in sediment A from three rivers and six regions in El Mina city

Portcom and Portpe correspond to commercial and fishing ports, respectively. The average standard deviation ($n=3$ per region) is less than 10%.

Linden and Rust (2006) and Khalaf et al. (2006) analyzed surface sediment samples (0-2 cm sediment at depths of 2-25 meters) on the seabed after the oil spill off the Lebanese coast in 2006. The concentration range of petroleum hydrocarbons in sediments is approximately 50 to $1,416 \mu\text{g.g}^{-1}$ p.s. There was a significant reduction in PAH levels between the measurements taken following the oil spill in 2006, that of Manneh et al. (2016) (732 ng.g^{-1} dw) and ours ($1,800 \text{ ng.g}^{-1}$ dw). This may be the result of the degradation of these molecules in the sedimentation chamber and water. Like soil, the biodegradation of polycyclic aromatic hydrocarbons can significantly occur in sediments through prokaryotic organisms and eukaryotic seaweed (Haritash and Kaushik, 2009). Due to oxygen being an important limiting factor (Zhang et al., 2006), microbial degradation in marine sediments is restricted, and marine sediments are mainly hypoxic; the range of the oxide layer ranges from a few millimeters in most open ocean sediments and eutrophic continental systems to several decimeters in some continental margins and non eutrophic continental systems (Cai and Sayles, 1996; Martin et al., 1998). However, polycyclic aromatic hydrocarbons can be degraded in anoxic sediments under denitrification conditions as long as the nutrients are not limited (Macrae and Hall, 1998); the use of nitrate ions as alternative electron acceptors for oxygen seems to activate the degradation of polycyclic aromatic hydrocarbons.

Polycyclic aromatic hydrocarbons can also be oxidized by ultraviolet radiation in illuminated areas - depending on environmental characteristics, in water bodies less than 1 meter to more than 50 meters below the surface. The

photodegradation of polycyclic aromatic hydrocarbons in water seems to be controlled by the distribution between dissolved/particulate phases, and therefore by the physical and chemical characteristics of the water, such as salinity, dissolved and particulate organic matter concentration, and pH value (Kong and Ferry, 2004; Nikkil ä and Penttinen, 1999; Oris and Tylka, 1990; Trapido et al., 1995). The presence of dissolved organic matter appears to have a strong inhibitory effect on the photodegradation of polycyclic aromatic hydrocarbons in water through radiation attenuation and/or extinction of molecular excited states (Nikkil ä and Penttinen, 1999; Oris and Tylka, 1990).

3.1.2 Time variations

By analyzing the temporal changes of polycyclic aromatic hydrocarbons, three annual sampling activities can distinguish two groups of locations:

- Throughout the dry and rainy seasons, there were six areas along the coast of El Mina city where concentration changes were minimal.

- The average concentration changes between samples during the dry season (August and October) and rainy season (January) were collected at three locations along three rivers (C, T, and A).

It should be noted that comparing sediment pollution levels between one season and another does not allow for observing temporal changes in sources. In fact, surface sedimentary materials can occasionally be reconstructed during different events (storms, dredging, biological disturbances, or other human disturbances), or continuously constructed through the dragging of sand or the resuspension of silt and ocean currents (Coulon, 2014).

Sites with greater concentration variability between dry and rainy seasons appear to exhibit greater spatial heterogeneity in polycyclic aromatic hydrocarbon concentrations and sediment physico-chemical characteristics (grain size). However, monitoring research over a longer time scale (6 years) can visualize the temporal variability of sources and uses.

3.1.3 Comparison with other websites

Compared with highly polluted sites in Hong Kong (Tam et al., 2001), Tanzania (Gaspare et al., 2009), Italy (Cardellicchio et al., 2007), and the United Kingdom (Vane et al., 2007), the polycyclic aromatic hydrocarbon values measured in sediments from three rivers and the El Mina coastal sites are considered to be mildly to moderately polluted. The values measured in coastal sites are at the same level and/or exceed, in most cases, those measured in sites receiving urban, agricultural and industrial discharges (Aldarondo-Torres et al., 2010; Jaffe et al., 2003; Lee et al., 2005; Liu et al., 2009; Samara et al., 2006; Yan et al., 2009). These values also exceed those measured by Manneh et al (2016) in surface sediments from 4 Lebanese ports (Tripoli, Jounieh, Dora and Tyre). This pollution is the result of the types of waste dumped for decades along rivers in addition to marine inputs. The maximum values measured in the port sites ($9,065 \text{ ng.g}^{-1} \text{ dw}$) far exceed those reported by Merhaby et al. (2015) in sediments from the port of Tripoli ($2,965 \text{ ng.g}^{-1} \text{ dw}$). This difference lies in the nature and granulometry of the sediment fraction analyzed.

Wagener et al (2012) reported that traditional PAH source diagnostic reports were not effective PAH source indicators; for example, biomass burning was assigned as a major source of pyrolytic PAH even though the catchment studied was highly industrialized and urbanized. They demonstrated that the petrogenic footprint cannot be detected if only the 16 EPA PAHs are determined. This study indicates the complexity of identifying the sources of polycyclic aromatic hydrocarbons when applied to chronic polluted environments; it is similar to the locations where untreated wastewater has been discharged for decades in our research.

In the sediment of Lake Manzala in Egypt, Barakat et al. (2012) inferred that the levels of pollutants in the areas mainly affected by urban landfills were significantly higher, indicating an important source of these compounds in

urbanized areas and demonstrating the results of the Abu Ali River coastal environment receiving leachate from the Tripoli landfill.

3.1.4 Toxicity

Due to the multiple sources and widespread presence of polycyclic aromatic hydrocarbons, these pollutants typically exist in the environment in complex mixtures. Many studies focusing on evaluating the toxicity of polycyclic aromatic hydrocarbon mixtures have shown that the toxicity of individual compounds is additive (Erickson et al., 1993; Swartz, 1999). In addition, the environmental matrix is more complex, containing many endogenous or exogenous minerals or organic molecules that may interact with each other. Especially, synergistic toxic effects were observed between metals and polycyclic aromatic hydrocarbon quinones (Flowers et al., 1997; Xie et al., 2007), opening the door to potential ecotoxicological effects of other emerging pollutants.

The carcinogenic and genotoxic effects of polycyclic aromatic hydrocarbons on organisms have been widely studied (Xu et al., 2016). The current literature confirms that polycyclic aromatic hydrocarbons are highly carcinogenic and highly toxic to benthic organisms (Nakata et al., 2014; Qu et al., 2018; Xiang et al., 2018). Table 1 presents the empirical sediment quality standard "SQG" that contributes to the overall assessment of toxicity of marine or coastal sediments.

Table 1. Empirical sediment quality standards (SQG) used to assist in the general assessment of toxicity of marine or coastal sediments (Along et al., 1998; Bmacdonald et al., 2000)

HAP	ERL ^a	ERM ^a	TEL ^b	PEL ^b
	en ng.g ⁻¹ de poids sec			
Naphthalene	160	2,100	34.6	391
Acenaphthalene	44	640	5.87	128
Acetylnaphthalene	16	500	6.71	88.9
Fluorine	19	540	21.2	144
Phenanthrene	240	1,500	86.7	544
Anthracene	85.3	1,100	46.9	245
Fluoranthene	600	5,100	113	1,494
Pyrene	665	2,600	153	1,398
Benzo (a) anthracene	261	1,600	74.8	639
Chrysene	384	2,800	108	846
Benzo (b) fluoranthene	-	-	-	-
Benzo (K) fluoranthene	-	-	-	-
Benzo (a) pyrene	430	1,600	88.8	763
Indeno [1.2.3-cd] pyrene	-	-	-	-
Dibenzo [a. b] anthracene	63.4	260	6.22	135
Benzo[ghi]Perilene	430	1,600	-	-
∑HAP	4,022	44,792	1,684	16,770

^aNaphthalene, acetylnaphthalene, acenaphene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (K) fluoranthene, benzo (a) pyrene.

^bNaphthalene, acetylnaphthalene, acenaphene, fluorene, phenanthrene, anthracene, fluorescein, pyrene, benzo (a)

anthracene, chrysene, benzo(a) pyrene.

From a toxicological perspective, it is widely believed that the biological effects of hydrocarbons in sediment begin to occur in the most sensitive organisms within a concentration range of 50 to 100 mg.kg⁻¹ dw. Among numerous sediment quality guidelines proposed since the 1990s, Long et al. (1998) and Swartz (1999) defined these criteria, which are frequently used to evaluate the toxicity potential of marine or estuarine sediments separately:

- The available ERL (effect range low) and ERM (effect range medium) values for 13 PAH^a
- Threshold effect level (TEL) and potential effect level (PEL) of 11 HAP^b

These standards are derived by compiling and statistically processing biological effect data of marine or estuarine benthic species observed in the laboratory or modeling site, as well as chemical characteristic data of sediments (different types of pollutants) in contact with these species. They allow for the differentiation of sediments with high probability (>ERM and PEL), potential (between ERL/TEL and ERM/PEL), or low probability (<ERL and TEL) toxic effects on biota based on chemical assays.

Swartz (1999) highlighted the good agreement between assessments made from different GQS when used in the case of mixing; it was thus able to conclude that there is indeed a cause and effect relationship between contaminant concentrations and the observed effects, and not a coincidence of correlation. As recommended by the various authors, GQS should be applied with caution as they are not perfect predictors of toxicity; it is preferable to supplement them with on-site biological monitoring and/or toxicity biological testing (Long et al., 1998).

Comparing the concentrations of polycyclic aromatic hydrocarbons measured in sediments from the Eastern Mediterranean analysis site with the empirical sediment quality standard "SQG" in Table 1 to assist in the general toxicity assessment of sediments, it was found that certain individual polycyclic aromatic hydrocarbons and their sum may pose toxicological risks to aquatic organisms. Sediments in coastal areas with the highest concentration of polycyclic aromatic hydrocarbons pose the greatest ecological risk. Sediments from the Abu Ali River port and coastal environment indicate that the concentration levels of polycyclic aromatic hydrocarbons between Tel and Pel may have toxic effects on aquatic organisms.

3.1.5 Identification of PAH sources

Different molecular ratios are used to determine the source of polycyclic aromatic hydrocarbons, such as the widely used and mentioned FLT/(FLT+Pyr), B (A) A/(B (A) A+Chr), Ant/(Ant+Phen), and Ind/(Ind+B (Ghi) P) ratios in literature. They are used as qualitative indices to distinguish between sources of contamination of pyrolytic and petrogenic origin in an environmental matrix (Budzinski et al., 1997; Baumard et al., 1998a, b; Raoux, 1991; Wang et al., 1999; Yunker et al., 2002).

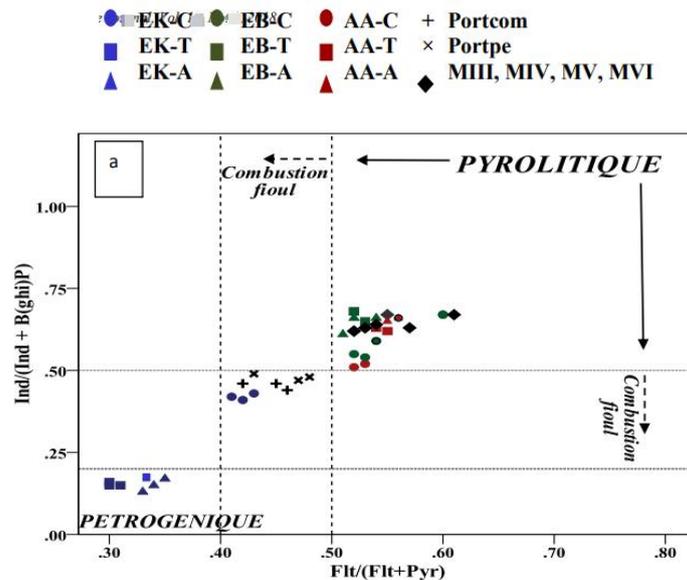
Similar to the study by Yunker et al. (2002), the molecular index ratios of different regions of three rivers (C, T, and A), coastal sewage discharge points (MIII, MIV, MV, and MVI), and port points (Portcom and Portpe) were graphically two by two correlated (always on the horizontal axis FLT/(FLT+PAYR)) (Figure 4).

The Ind/(Ind+B(ghi)P) ratio (Figure 4a) shows a marked petroleum input upstream of the river EK, with a gradient that decreases towards the coast. The three river zones of EB and AA, as well as M, are not differentiated by the combination of the two indices. The Ant/(Ant+Phen) ratio (Figure 4b) provides additional information and makes it possible to clearly distinguish between zone A and T of the AA and EB rivers and zone C of these two rivers, which are at the same level as EK sediments. The sum of the values obtained when calculating the Ant/(Ant+Phe) ratio in sediments in the coastal areas of the three rivers, the transitional and upstream areas of the El Kebir River and the sewage discharge areas of the city of El Mina is less than 0.1. This report highlights a marked petrogenic origin that seems relatively

homogeneous: the predominance of the Phe isomer over the more thermodynamically stable Ant isomer. This homogeneity of values indicates that the PAHs present at these sites have a very specific common origin, which is the fuel dumped in 2006. The combination of Flt/(Flt+Pyr) and B(a)A/(B(a)A+Chr) ratios (Figure 4c) makes it possible to discern in the sediments of these sites an input via combustion of wood, plants and coal [$Flt/(Flt+Pyr) > 0.5$ and $0.2 < B(a)A/(B(a)A+Chr) < 0.35$], as well as a mixed input (petroleum and pyrolytic) upstream and in the transition zones of the El-Bared River. The pollution along the El Bared site was caused by the supply of polycyclic aromatic hydrocarbons through the Deir Amar thermal power plant.

Therefore, the analysis of the commonly used molecular ratios indicates that in the upstream and transition zones of El Bared and Abou Ali rivers, the pyrolysis origin is higher than the rock source origin of polycyclic aromatic hydrocarbons. In the coastal environment of these two rivers, rock sources dominate the El Mina coast and the entire El K é bir River, but the reported values vary within a relatively large range, indicating different pyrolysis characteristics. In El Kebir, difficulties in controlling parts of the border between Lebanon and Syria have led to severe pollution of the upper reaches of the river and the transition zones by smuggling trade, especially polycyclic aromatic hydrocarbons produced from oil (IDRC, 2004). The port location shows a combination of pyrolysis and rock source, which is clearly different from all other locations.

In addition to mainland and maritime activities, on July 13 and 15, 2006, the fuel tank of Jiyeh Thermal Power Plant located 30 kilometers south of Beirut, Lebanon, on the east coast of the Mediterranean Sea was bombed, causing a large amount of oil leakage, which seems to be the cause of pollution at the studied coastal location.



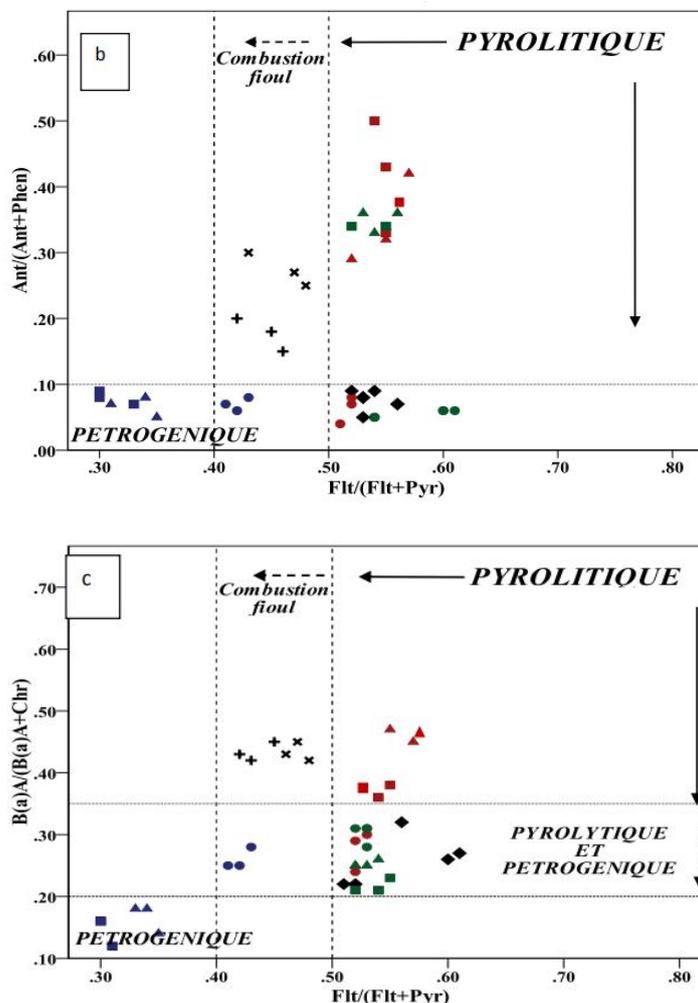


Figure 4. Determine the sources of polycyclic aromatic hydrocarbons in sediments from three rivers (C, T, and A zones), coastal locations (MIII, MIV, MV, and MVI), and port locations (Portcom and Portpe) using different concentration ratios

4 Conclusion

The oil spill incident that occurred after the Jiyeh thermal power plant oil tank explosion in southern Lebanon in 2006 left major pollution marks along the Eastern Mediterranean coast and at the mouths of the three rivers studied. In terms of land investment, the pollution level of river sites is lower than that of coastal sites. Sediments from the coastal areas of three rivers, El Mina coastal sediments, and port sediments have a high proportion of pyrolysis and rock derived polycyclic aromatic hydrocarbons. The sedimentary compartment thus constitutes a sink and a major stock of PAHs for the coastal environment, which can be remobilized towards the water column during major agitation of the water masses or anthropogenic disturbances. Comparing the levels of polycyclic aromatic hydrocarbon pollution in rivers and coastal sediments in the Eastern Mediterranean with the empirical sediment quality standard "SQG" to assist in the general assessment of toxicity in marine or coastal sediments, the toxicity issue of these sediment particles has been raised, which is crucial for monitoring the environmental quality of coastal environments and transition zones.

This work could be of paramount importance for the Eastern Mediterranean region, and more particularly for Lebanon, a country which, although a signatory to the Barcelona Convention for the protection of the Mediterranean Sea and involved in monitoring the quality of its marine environment, has until now suffered from discharges of various types of untreated effluent along its coasts in the absence of industrial and urban wastewater treatment plants.

Conflicts of interest

The author declares no conflicts of interest regarding the publication of this paper.

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