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## ASSESSMENT OF PERSISTENT ORGANIC POLLUTANTS IN SURFACE SEDIMENTS ALONG LEBANESE COASTAL ZONE

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### Abstract

The levels of some persistent organic pollutants (POPs) along the Lebanese coastal zone (LCZ) were assessed by collecting 15 surface sediments from five hotspot stations. Such stations were influenced by various industrial units, riverine input, and touristic activities. The levels of polycyclic aromatic hydrocarbons ( $\Sigma 16$ PAHs), their methylated

derivatives ( $\Sigma 18\text{Me-PAHs}$ ), and polychlorinated biphenyls ( $\Sigma 28\text{PCBs}$ ) were in the range of 537-3773  $\mu\text{g.kg}^{-1}\text{dw}$ , 187 -1541  $\mu\text{g.kg}^{-1}\text{dw}$ , and 143-303  $\mu\text{g.kg}^{-1}\text{dw}$  respectively. Significant contamination was found at Beirut Port that is surrounded by a densely populated area and is subjected to multidisciplinary activities. Source identification of PAHs was confirmed by using the diagnostic ratio of PAHs with low molecular weight and high molecular weight (LMW/HMW). For PCBs, LCZ is polluted by higher chlorinated congeners with 4 to 9 chlorinated atoms generated from volatilization and combustion processes. Toxicity and biological risks were assessed using toxic equivalent quantity (TEQ<sub>carc</sub>) and sediment quality guideline quotient (SQG<sub>q</sub>).

**Keywords:** POPs, PAHs, PCBs, Sediments, LCZ and SQG<sub>q</sub>.

Lebanon is a typical case of most coastal areas of the developing countries in the region. A wide range of anthropogenic activities are contributing to water pollution of the Lebanese coastal zone (LCZ) and overall environmental degradation. The LCZ is suffering from uncontrolled urban sprawl and unplanned development (El Asmar et al., 2014). The intensive coastal urbanization involves the concentration of industrial activity along the coast, which increases the release of untreated sewage and industrial effluent into sea, leading to a threat to marine ecosystem (Green Peace, 2007). There are more than 53 network pipelines of wastewater on the coast of Lebanon, and several industrial plants located on LCZ hosts four commercial ports and over 15 fishing harbors, dozens of sea pipelines for petroleum imports, three fuel power plants, and a series of various industries and factories (El Asmar et al., 2014). In addition, the inland activities contribute to the pollution of the Mediterranean Sea by drainage pollutants along the rivers. Moreover, the Lebanon oil spill event caused by Israeli air raids in 2006 is one of the biggest environmental catastrophes in the Eastern Mediterranean Sea and was the most visible environmental impact of the war, resulting in both short- and long-term threats to the coastal marine environment of Mediterranean Sea (Green Peace, 2007). Coastal sediments are one of the major sinks of the mixtures of these persistent organic pollutants (POPs) with levels higher 1000 times than water column (Luca et al., 2005), causing serious problems due to their toxicity, persistence to biodegradation and their ability to accumulate in the biota up the food chain (Peachey, 2003; Guzzella et al., 2005; Qiu et al., 2007; Morillo et al., 2008; Wade et al., 2008; Tekin & Pazi, 2017; Vitali et al., 2019; Mennillo et al., 2020). Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are widespread and ubiquitous organic contaminants in marine environment (Jonsson et al., 2003; dos Santos Rogrigues et al., 2018; Huang et al., 2012; Soukarieh et al., 2018; Helou et al., 2019; Merhaby et al., 2019) and may be most commonly associated with oil spills and/or urban and industrial discharges (King & Chou, 2003). Moreover, limited water exchange makes the Mediterranean Sea very sensitive to the build-up of these pollutants (Green Peace, 2007). Sediment remobilization has been identified as a key process of reintroducing POPs to the water column, which pose a potential risk to the wildlife ecosystem and human health (Jurado et al., 2007; Lohmann et al., 2007; Huang et al., 2011). Therefore, because of its ecological importance, the evaluation of coastal sediment quality constitutes an important area of research (Silva et al., 2004; Usero et al., 2008).

From a dynamic point of view, semi-enclosed basins such as ports and estuaries where chronic pollution from shipping occurs and other industrial activities requires more detailed fingerprinting of different contaminant sources (Zahreddine et al., 2004, Vitali et al., 2019). In this study, the contamination levels of 16 PAHs, 18 Me-PAHs and 28 PCBs in 15 surface sediments samples collected from five potential hotspot zones have been investigated. The potential toxicological effects were evaluated by comparison with sediment quality guidelines levels (SQGs). The study provided a first baseline data set to improve our understanding about the status of the Lebanese coastal ecosystem and stimulate policy makers to achieve an integrated coastal zone management (ICZM).

LCZ is a narrow and discontinuous strip formed of river-deposited alluvium and marine sediments, which alternate with rocky beaches and sandy bays and extends over 220 km along the Eastern Mediterranean Sea (Zahreddine et al., 2004; Grean Peace, 2007; UNEP, 2007). Lebanese coasts are being destroyed and replaced with beach resorts, large commercial facilities, industrial units and harbors (Zahreddine et al., 2004). This intensive anthropogenic activity is a potential source of coast pollution. The sampling stations were selected to cover LCZ with various industries and estuaries, particularly those influenced by intense shipping, freshwater input and touristic activities closed to several hotspots adjacent to the LCZ. These stations represent a wide range of environmental conditions in particular at ports and bays where the remobilization of coastal sediment can be occurred frequently. They cover about 110 km of Lebanese coastline extending from Jiyeh to Tripoli city (Eastern Mediterranean Sea, Lebanon) (Fig.1).

Fifteen surface sediments (top 5-10 cm) were collected from five sampling stations including; the commercial Port of Beirut, the Port of Jiyeh Power Plant, Abou Ali estuary, Touristic beach in Chekka bay, and Touristic beach in Jounieh bay (Fig.1). The sampling was performed in May 2014, and the GPS coordinates and other characteristics of the studied sites are presented in Table 1. Each sample was homogenized before being transferred into pre-calcinated aluminum containers capped with aluminum foils. Three surface sediments samples were collected from each station at different depth below water surface. Sediment samples were transported in the laboratory and dried at room temperature in a laminar hood.

The samples were analyzed for 16 PAHs, 18 Me-PAHs and 28 PCBs including 12 dioxin-like PCBs (PCB-DL) and the 7 indicators PCB (PCBi). The extraction, purification, and instrumental analysis for PAHs, Me-PAHs, and PCBs quantification were carried out

according to the procedure reported by Net et al. (2014) and Merhaby et al. (2015). Final extracts were analyzed by using a Varian 3900 gas chromatograph (GC) equipped with a deactivated fused-silica guard column (5 m, 0.53 mm i.d.) and a fused-silica capillary Phenomenex XLB (60 m length, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS). The GC-MS conditions have been reported by Merhaby et al. (2015) and Rabodonirina et al. (2015, 2019).

Mixed standard solutions of PAHs and Me-PAHs were purchased from Restek Corp (Bellefonte, PA, USA). PCBs standard solution was obtained from Accustandard Inc. (New Haven, CT, USA). Tetrachloronaphtalene (TCN), 2,3,3',5,6-tetrachlorobiphenyl (PCB112) and octachloronaphtalene (OCN), used for PCB quantification, were purchased from Dr Ehrenstorfer (Augsburg, Germany). Deuterated internal standards for PAHs and Me-PAHs (acenaphthene-d10 (A-d10), naphtalene-d8 (N-d8), perylene-d12 (Per-d12), phenanthrene-d10 (Phe-d10) and pyrene-d10 (Pyr-d10)) were provided by LGC-Promochem (Middlesex, UK). HPLC-grade solvents were purchased from Dislab (France). Ultrapure water (Milli-Q) was produced by a Millipore apparatus with 18.2  $\text{M}\Omega\cdot\text{cm}^{-1}$  resistivity. Merck silica gel 60 (70-230 mesh ASTM) activated at 450°C was heated at 120°C for 12h prior to use. Glassware was systematically washed with detergent (Decon, East Sussex, UK), rinsed with ultrapure water and acetone and finally dried at 120°C prior to use. Each analysis was carried out by triplicate for each site at different depth below water surface. For the quantification of PAHs, Me-PAHs and PCBs, the four-point internal calibration method was used. Deuterated Internal standards were chosen in order to better fit to the properties of targeted contaminant groups and were used in calculations for quality control of the data. The limits of quantification (LOQ) were estimated as ten times the baseline of blank chromatograms and were confirmed by experimental analysis. LOQs were determined in the range of 0.3-5, 18-38 and 0.5  $\mu\text{g}/\text{kg dw}$  respectively for PAHs, Me-PAHs and PCBs (Rabodonirina et al., 2015). The accuracy of the analytical procedure for the extraction of PAHs and Me-PAHs was reported previously by Net et al. (2014).

The sums of PAHs concentrations ( $\sum_{16}\text{PAHs}$ ), 18 Me-PAHs ( $\sum_{18}\text{Me-PAHs}$ ) and 28 PCBs ( $\sum_{28}\text{PCBs}$ ) for each station are reported in Table 2. Sediments from Beirut Port exhibited significantly higher concentrations of  $\sum_{16}\text{PAHs}$  (3773  $\mu\text{g}\cdot\text{kg}^{-1}\text{dw}$ ) (Fig. 2A). Beirut Port is the main important harbor in Lebanon and is one of the largest and busiest ports on Mediterranean Sea due to its role in the maritime trade between East and West. It has been serving as the capital of Beirut for shipping, transportation, and fishery activities for

the past several hundred years. High level of PAHs at Beirut Port may be due to the multiple activities in this harbor. Loading and unloading operations, shipping, transportation, fishery activities, industrial effluents, and ship and urban discharges are the main sources of PAHs contamination, and these activities are intense in Beirut Port. Manneh et al. (2016) found the  $\Sigma$ PAHs in sediments ranged from 1.22 to 732  $\mu\text{g}/\text{kg}$  were in general lower than the ones obtained in this study and by Merhaby et al., (2015) with PAHs concentrations ranging from 552 to 3773  $\mu\text{g}/\text{kg}$  and 507 to 2965  $\mu\text{g}/\text{kg}$ , respectively. This discrepancy could be due to the selected studied sites and sampling strategies. For example, the sampling stations chosen in this study were selected very close to the shore near the sources of pollution compared to sampling points selected by Manneh et al., (2016) at distance varied between 25 to 780 m from the shore.

According to Baumard et al. (1998a), the classification of PAHs pollution levels was as follows: low 0-100 ng/g; moderate >100-1,100 ng/g; high > 1,100-5,000 ng/g; and very high > 5,000 ng/g. Based on this classification, we suggest that it could be considered as moderate for all studied sites except for Beirut Port which is highly polluted with PAHs. These results are similar to those reported by Manneh et al., (2016) for Tripoli, Jounieh, Dora, and Tyre. However, Beirut Port was not explored by Manneh et al. (2016).

Concerning the  $\Sigma_{18}\text{Me-PAHs}$  along LCZ, the average was determined as 2617  $\mu\text{g}\cdot\text{kg}^{-1}\text{dw}$  with the range of 187-11541  $\mu\text{g}\cdot\text{kg}^{-1}\text{dw}$ . Sediments from Beirut Port also exhibited significantly higher concentrations of  $\Sigma_{18}\text{Me-PAHs}$  (11541  $\mu\text{g}\cdot\text{kg}^{-1}\text{dw}$ ) followed by the sediments from Port of Jiyeh Power Plant (731 $\mu\text{g}\cdot\text{kg}^{-1}\text{dw}$ ) (Fig. 2A). High level of Me-PAHs in Beirut Port may due to chronic exposure originated from harbor activities such as ship discharges and ships maintenance, oil spills accidents, oil leakage during oil supply for fishery boats and harbor effluents (Lamparelli et al., 1993).

For PCBs, the  $\Sigma_{28}\text{PCBs}$  is presented in Figure 2A. 24 PCBs congeners (PCBs 28, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 167, 169, 170, 180, 187, 189, 195, 206, and 209) were quantified for each sediment sample collected from five sampling stations along LCZ. The  $\Sigma_{28}\text{PCBs}$  ranged from 143 (Jounieh Bay) to 1303  $\mu\text{g}\cdot\text{kg}^{-1}\text{dw}$  (Beirut Port) with an average of 506  $\mu\text{g}\cdot\text{kg}^{-1}\text{dw}$ . High-level  $\Sigma_{28}\text{PCBs}$  at Beirut Port might be due to the emission of PCBs from paints, old equipment, or materials used in some vessels particularly during the activities of ships maintenance (shipyard) and might be associated with the use of capacitors and transformers in the industrial area surrounding this harbor. Indeed, PCBs can originate from shipping and industrial activities (Bícego et al., 2006; Hong et al., 2005, 2006). Similar results were reported for

the Korean coastal areas (Duan et al., 2013). Hence, we suggest the shipping and industrial activities combined with low local hydrodynamics as possible sources of the PCBs accumulation in the sediments at Beirut Port basin.

Among these 28 PCBs, 7 PCBs (CB 28, 52, 101, 118, 138, 153 and 180) were known as PCBs indicators ( $\Sigma_7\text{PCBi}$ ) due to their abundance in the environment and 12 congeners (CB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189) were called PCBs dioxin-like ( $\Sigma_{12}\text{PCB-DL}$ ) due to their high toxicity, persistency in the environment and their potential health effects (Kimbrough et al., 2010; Tanabe and Minh, 2010; WHO, 2018). Indirect PCBs exposure from environment can cause neurobehavioral effects and development in children (Jacobson & Jacobson, 1996; Korrick, 2001), memory and learning impairment in older adults (Schantz et al., 2001), endocrine-mediated effects including shortened menstrual cycle (Mendola et al., 1997), and other nonspecific reproductive effects (Ross, 2004). Direct occupational or accidental exposures can cause chloracne and other effects related to chronic dermal and ocular irritation (James et al., 1993). In this study, the  $\Sigma_7\text{PCBi}$  were found in the range of 7.9 - 575  $\mu\text{g.kg}^{-1}\text{dw}$  and the  $\Sigma_{12}\text{PCB-DL}$  were found in the range of 25.8 – 989  $\mu\text{g.kg}^{-1}\text{dw}$ . Figure 2B shows the  $\Sigma_7\text{PCBi}$  and  $\Sigma_{12}\text{PCB-DL}$  for the five sampling stations selected along LCZ. The highest concentrations for both  $\Sigma_7\text{PCBi}$  and  $\Sigma_{12}\text{PCB-DL}$  were observed at Beirut Port with 575 and 989  $\mu\text{g.kg}^{-1}\text{dw}$  respectively (Fig. 2B). The  $\Sigma_{12}\text{PCB-DL}$  which are the highly toxic congeners were dominant in all the stations except for Port of Jiyeh power plant (Fig. 2B). Beside the harbor activities which lead to a large content of PCB-DL in sediments, Abou Ali estuary showed also an important concentration of PCBs. PCB-DL represented 81.6 %, which indicate that this river is highly affected by anthropogenic activities (Massoud et al., 2006). In fact, Abou Ali River flows through an urbanized region with high-density population (Tripoli City). Many industries comprise small facilities scattered throughout the river including car repair workshops, food processing establishments, furniture manufacturing and woodcrafts, restaurants, various shops (CES, 2001) and three hydroelectric plants along the river with a combined nominal capacity of 12.1 MW (MOE, 2001). Plus, the Northern coastal area of the river mouth is targeted to become the industrial zone of the Tripoli district where a major wastewater treatment plant which, at present, still not operates in the full capacity of 40,000  $\text{m}^3$  and various industrial units were constructed (JICA & CDR, 2001). Therefore, the combination of different pollution sources including solid waste dumping sites in an open area of 65,000  $\text{m}^2$  located on the coast near the mouth of Abou Ali River (CES, 2001),

the dumping of wastes, discharging of waste water and industrial effluent directly to the river with the average annual rate of 262 million m<sup>3</sup> (MOE, 2001; Doong et al., 2008) led to this organic contamination by these highly toxic congeners (Greanpeace, 2007; Kabbaraa et al., 2008). Abou Ali River acts as a transit zone where the contaminants are transported from the rivers to the sea (Oros and Ross, 2004; Wang et al., 2008).

The highest content of PAHs, Me-PAHs, and PCBs was detected at Beirut Port. This contamination may be due to both urban and industrial activities and the intensive sedimentation (Konat&Kowalewska, 2001). Indeed, as the Beirut Port has limited water circulation and low exchange with the open sea, the closed basins are mainly responsible for this localized high pollution in comparison with other stations (Luca et al., 2004; Bicego et al., 2006). Beirut Port was contaminated by PAHs, Me-PAHs and PCBs higher than the values determined in Tripoli harbor by Merhaby et al. (2015). However, the concentrations of PAHs, Me-PAHs and PCBs in sediments samples show a random distribution between the samples collected at different depths below the water column at each station. The contamination level increased with the increase of depth at SCB, SPB and SAE stations for PAHs, Me-PAHs and PCBs respectively (table 2). This random distribution may be influenced by multiple factors including potential sources, sorbing phases, geological composition of sediments (mainly consist of sandy clay), meteorological conditions (precipitation patterns, wind speed, temperature), circulation patterns (currents and wind waves), sedimentation process, hydrodynamic transportation and surrounding food web structure, (Guo et al., 2003; Lohmann et al., 2007, Vitali et al., 2019).

The majority of PAHs were detected and quantified in all samples except for sediments collected from Jounieh Bay were the concentrations of PAHs with 6-rings were unquantified. The composition profile pattern for (A) PAHs, (B) Me-PAHs and (C) PCBs in samples collected from five sampling stations along LCZ are shown in Figure 3.

PAHs with medium molecular weight (MMW-PAH) and high molecular weight (HMW-PAHs) with four-, five- and six- rings were the most abundant at Abou Ali estuary, Chekka Bay and Beirut Port. In contrast, PAHs with low molecular weight (LMW) with three rings were dominant at Jounieh Bay and Jiyeh power plant. High levels of four- and five-rings hydrocarbons are distinctive of mixtures formed by the combustion of fossil fuels (Gogou et al., 2000). The results indicate that there are potentially multiple sources of PAHs contamination in each station, mainly related to harbor, touristic and fishery activities. However, LMW are more volatile and degradable in the environment

(Quantin et al., 2005; Merhaby et al., 2015, Vitali et al., 2019) than HMW, so their concentration at Jounieh Bay and Port of Jiyeh power plant indicate the presence of continuous input sources at these stations. LMH-PAHs (two- and three-rings) are produced from petroleum products, fossil fuels and biomass incomplete combustion at low to moderate temperature and natural digenesis, while MMW and HMW-PAHs (four- or more ring structures) are produced at high temperature (Yuan et al., 2001; Mai et al., 2002). Hence, each PAH has a proper potential hazardous effect; PAHs with four- to seven-rings are highly mutagenic and PAHs with two- or three-rings are highly toxic (Fernandes et al., 1997; Law et al., 1997; Zhou &Maskaoui, 2003; Nakata et al., 2003). For Me-PAHs, the results show that Me-PAHs with 3-rings were observed in majority for samples collected from Abou Ali estuary and Beirut Port. However, Chekka Bay and Jounieh Bay were dominated by 2-rings Me-PAHs (Fig. 3B). No significant variation was observed concerning the composition of Me-PAHs with 2, 3 and 4-rings for samples collected from Jiyeh Port (Fig. 3B). It is interesting to note that Me-PAH a tracer of petroleum input confirming the presence of oil residues from multiples sources at all investigated stations.

Low PCBs levels were observed for all sampling stations (Fig. 3C). There is a dominance for the distribution of higher chlorinated PCBs which can be explained based on several environmental processes. Indeed, two major processes may affect the fate and composition of PCBs in water, dissolution and anaerobic dechlorination, causing opposite trends in homolog distribution pattern (low, medium and high Cl CBs). The anaerobic dechlorination process is characterized by a decrease in higher chlorinated congeners and the increase in lower congeners as a result of microbial dehalorespiration (Li et al., 2009). In water, these low congeners tend to be more susceptible to the dissolution loss process (Li et al., 2009). In the atmosphere, due to their high solubility and volatility, lower chlorinated PCBs can be easily degraded by hydroxyl radicals (Mandalakis et al., 2003), whilst the higher chlorinated congeners are more persistent in the environment (Ross, 2004). Moreover, a supplementary phenomenon was reported by Hornbuckle et al. (2004), suggesting that PCBs concentration tends to be higher when important sediment resuspension event induces a vertical fractionation of PCBs congeners, leading to the loss of lower chlorinated PCBs compared with higher ones (Li et al., 2009). Based on our results, we suggest that the dissolution process may affect significantly the PCBs distribution and composition pattern leading in consequence to a potential risk for wildlife and human health based on the possibility that these congeners

are absorbed by mussels and fishes (Ross, 2004). Recent studies have shown that each PCBs congener has a different biological activity and toxicity due to the number and position of chlorine atoms in its structure. Although these different processes controlling PCBs behavior in the environment, large amount of high chlorinate PCBs at Beirut Port indicates that these contaminants might be unintentionally released from human activities thus transported primarily through atmospheric processes including wetfall, dryfall and river inputs and water-air exchange (Strachan & Eisenreich, 1990; Li et al., 2009).

Sources of anthropogenic PAHs in coastal marine sediments belong to two processes: petrogenic and pyrogenic, based upon the predominance of different PAHs congeners. Pyrogenic sources originate from combustion processes (e.g., fossil fuel combustion, forest fires, shrub and grass fires) characterized by abundance of HMW PAHs (Wang et al., 1999). While petrogenic sources are closely related to the direct release of crude and refined petroleum products (e.g., oil spills, power plant, oil pipes, urban runoff, oil seeps and road construction materials) (Luca et al., 2004) characterized by abundance of LMW-PAHs and methylated PAHs (Simpson et al., 1996; Fernandes et al., 1997; Zhou et al., 1998; Barakat et al., 2011). Therefore, several molecular and isomeric pair ratios of PAHs were used in order to survey their sources. The origins of PAHs in sediments along LCZ are reported in Table 3: (A) Characteristic values and (B) source identification based on selected molecular, isomeric and homologue methyl-PAHs ratios for petrogenic and pyrogenic origins of PAHs (Baumard et al., 1998; Budzinski et al., 1997; Yunker et al., 2002).

The use of molecular ratio Flu/Pyr (Budzinski et al., 1997; Magi et al., 2002) alone could lead to a misleading diagnostic of PAH sources according to what suggested by Raoux (1991), and Baumard et al. (1998a). As shown in Table 3B, the results of PAH molecular and isomeric ratios give an inconsistent picture of PAHs origins so these four diagnostic ratios seem to be inadequate for the differentiation of hydrocarbon origins in our case of the LCZ sediment samples. The dominance sources of PAHs are not similar for all used diagnostic ratios at each station, except for Abou Ali estuary, where all ratios used show the predominance of pyrogenic sources. Indeed, recent studies show that pyrogenic sources can be characterized by the predominance of parent compounds with four or more aromatic rings derived during combustion. In contrast, petrogenic sources contain only two and/or three aromatic ring compounds derived from the direct discharges of petroleum and its products (Barakat et al., 2011; Chen & Chen, 2011, Vitali et al., 2019).

Therefore, a ratio of LMW to HMW PAHs was used to identify between these two sources. The ratio LMW/HMW  $<1$  indicates the pyrogenic sources and the ratio  $>1$  indicates the petrogenic sources of PAHs in sediments (table 3A) (Budzinski et al., 1997; De Luca et al., 2005). In Table 3B, the results of this ratio (LMW/HMW) show that combustion was the predominant source of PAHs at Abou Ali estuary, Chekka Bay and Beirut Port while the petroleum input was the predominance source at Jounieh Bay and Port of Jiyeh power plant. The ratios of methylated PAHs compounds (A-PAHs)/Parents PAHs (P-PAHs) have been plotted versus LMW/HMW ratio to show the predominant sources of PAHs (Fig. 4). It is interesting to note that the results of the LMW/HMW ratio comply with the composition profile of PAHs described previously in this paper. Therefore, the comparative evaluation between the molecular/isomeric pairs ratios and the LMW/HMW ratio indicates that this ratio can be considered a reliable tool for discriminating between petrogenic and pyrogenic origins of PAHs (Sicre et al., 1987; Budzinski et al., 1997, Vitali et al., 2019).

LCZ is subjected to high contamination by PAHs mainly due to the urbanization and industrial development in this zone. For Beirut Port, combustion was defined as the predominance sources of PAHs mainly resulting from ships engine emissions, port equipment (e.g. winches, forklifts), maritime transport or shipping activities, vehicles traffic (highway), diesel trucks (Transit activities) and dust generated from rehabilitation and construction activities (Mostert et al., 2010; Tobiszewski&Namieśnik., 2012; Feng et al., 2012; Borgie et al., 2015). Moreover, the capital Beirut has a high density of population suggesting that exhaust emissions from vehicles and burning of wood and biomass may contribute to PAHs pollution in this area as well as for Abou Ali River, which passes through Tripoli city, the second largest city in Lebanon. In fact, POPs prone to long range transport via atmospheric route which has been identified as the key global dispersal mechanism for most legacy POPs including PAHs and PCBs. According to Wania (2003) these POPs can be classified as flyers, multi-, single hoppers and swimmers. A number of emerging POPs may not fall into the same multimedia region (Lohmann et al., 2007). Whereas, PAHs act as "single hoppers" suggesting that Beirut Port can be affected by the emissions released from surrounding industries and power plant such as the case of Jiyeh power plant which is located at 30 km away from the capital. For Chekka Bay, the dominance of combustion process can be explained by the presence of two cement factories. In addition to being an industrial leader on the Lebanese market, the company is also a prominent worldwide cement exporter, serving

the Levant, Africa and occasionally Europe. Harbor activities are reserved essentially for the import of coal, petroleum products, slag, and gypsum and the export of clinker and cement. Their location on the coast have an important access to the regional markets in the Mediterranean basin through this port leading to an important production, transport and shipping activities which often increase the risk of pollution by toxic chemicals in particular PAHs released during combustion process and the emission of coal/coke dust. Although there is presence of these important sources of pollution at Chekka Bay, the level of contamination is less than that at Beirut Port, reaching  $552 \mu\text{g}\cdot\text{kg}^{-1}\text{dw}$ ; this area is well covered by long trees and high mountains regions that could play as a traps for these contaminants (Grimalt et al., 2001; Daly & Wania, 2005). For Port of Jiyeh power plant, the petrogenic sources was the predominance sources of PAHs in sediments mainly released from the direct inputs of petroleum product in particular the oil spillage event occurred during the conflict with Israel in July 2006, shipping activities, oil loading/unloading operations, oil leaks or spills from pipelines, tanks and ships, ships discharges and cooling water taken from the Sea and let into the Sea (Luca et al., 2004; Huang et al., 2011, Vitali et al., 2019). For Jounieh Bay the predominance of petrogenic sources mainly related to the urban runoffs, sewage discharges, fishery and touristic activities where many boats travelling in the bay and yachts center; hence, there are many nonpoint sources contributing to petrogenic PAHs contamination (Zhou & Maskaoui, 2003). Our results are in good agreement with the PAHs characterization of others harbors and marinas in the Western part (Luca et al., 2004; Vitali et al., 2019) and in the Eastern part (Barakat et al., 2011, Merhaby et al., 2015, Manneh et al., 2016; Vitali et al., 2019) of the Mediterranean Basin.

Sources identification of PCBs in environment is a challenge, PCBs data are the most highly diversified and difficult to interpret (Konat & Kowalewska, 2001) because no diagnostic ratios of PCBs congeners can be found in the literature similar to that used for PAHs. Following the ban on PCBs production in 1970s, PCBs are still present at trace levels in marine environment (Ross, 2004). Therefore, we should note that some equipment and materials containing PCB are still in use in some region in the world (Ross, 2004) (e.g. capacitors, concrete coatings, and double framed glazing windows, vessels paints, exterior paint from building façades and building materials (Andersson et al., 2004). Moreover, it is interesting to mention that continuing PCBs emissions in densely populated areas (Jaward et al., 2004) not only attributed to the volatilization processes from soils, equipment and building materials but also formed during thermal

processes (Schoonenboom et al., 1995; Konat&Kowalewska, 2001; Ishikawa et al., 2007; Lohmann et al., 2007) mainly related to industrials (Hong et al., 2005; Aries et al., 2006; Liu et al., 2009), waste incineration (Shibamoto et al., 2007), vehicle exhaust (Brož et al., 2000) and combustion of organic matter (Kjeller&Rappe, 1995; Rose & Rippey, 2002; Rose et al., 2004). PCBs are classified as multi-hoppers compounds (Wania, 2003, 2006). Therefore, the detection of these pollutants in coastal sediments suggests an efficient delivery of these multi-hoppers compounds via atmospheric deposition due to gaseous exchange across the air/water interface process, dry deposition of airborne particulate matter, by rainfall, storm water runoff (Dickhut & Gustafson, 1995; Dickhut et al., 2000; Tsai et al., 2002; Oros et al., 2006) and via riverine input (Konat and Kowalewska, 2001).

Whereas, PAHs and PCBs have similar physico-chemical properties like hydrophobicity, persistence, long-range transport and are removed from water column by sedimentation, accumulation into food webs and volatilization processes (Lohmann et al., 2007). For these reasons, Fernández et al., (2012) and Duan et al., (2013) suggest to consider the correlation between PAHs isomers and PCBs congeners for sources identification. The composition of PCBs in sediments can provide the information on environmental origin, transport and fate processes (Li et al., 2009). 5 Cl CBs was produced as paint additive (Mai et al., 2005) so the predominance of 5 Cl CBs (56.95 %) detected in the sediments of Beirut Port and other ports indicates that paint constitute one of the important sources of PCBs. Therefore, the rehabilitation and demolition of the surrounding buildings mainly are the major source of PCBs in coastal sediments at Beirut Port (Jartun et al., 2009). Other PCBs congeners with  $\geq 6$  Cl atoms detected in sediments at Beirut Port station could be originated from unintentionally atmospheric deposition released from port equipment, generators, ships, vehicles and trucks exhaust. Jiyeh power plant contribute to the dominance of 4-6 Cl CBs and the cement factories at Chekka Bay contribute to the dominance of 7 and 9 Cl CBs. Fishery and touristic activities at Jounieh bay resorts lead to the dominance of high chlorinated PCBs with 8-9 Cl CBs which release probably from fishery boat, yachts engine and vehicle exhaust emissions surrounding. The riverine input of Abou Ali estuary with the predominance of 7 Cl CBs which may be related to continuing diffusive atmospheric emissions in populated area (Jaward et al., 2004c) unintentionally released from vehicles exhaust and the combustion of organic matter (Kjeller&Rappe, 1995; Rose & Rippey, 2002; Rose et al., 2004) which occurred frequently in Tripoli plain and villages where the river pass through. PCBs contamination

is linked to population density at Beirut Port, which is located in the capital. Based on these findings, PCBs contamination is not only the historic problem but there may have continuous emissions from urban and industrial regions along LCZ leading to this high contamination of coastal sediments. The current source of PCBs could be volatilization from paints and building materials as the case of Beirut Port, and combustion process at Chekka Bay, Jiyeh power plant and Abou Ali estuary (Hsu et al., 2003; Uraki et al., 2004).

The evaluation of potential toxicity was performed based on the calculation of total concentration of potentially carcinogenic PAHs (C-PAHs: BaA, Chr, BaP, BbF, BkF, IP, and DBA) (Nadal et al., 2004; Qiao et al., 2006; Sprovieri et al., 2007; Lee et al., 2010; Tian et al., 2013) and PCBs-DL. The concentrations of C-PAHs and PCBs-DL at all investigated stations are presented in Table 4. The highest C-PAHs was determined at Beirut Port reaching 2370  $\mu\text{g.kg}^{-1}\text{dw}$  and accounting for 62.8 % of total PAHs. The lowest C-PAHs concentration was found at Port of Jiyeh power plant reaching 125  $\mu\text{g.kg}^{-1}\text{dw}$  and accounting for 22.7 % of total PAHs. Among these, C-PAHs, BkF and IP were the predominance compounds at all stations. Except at Beirut Port, BaA and BbF was the predominance C-PAHs. PCBs-DL are classified into three categories: non-ortho PCBs, with high concern of dioxin-like effects; mono-ortho substituted PCBs, with a weak ability to produce dioxin-like effects; and multiple-ortho substituted PCBs, with no dioxin-like effects (Ma et al., 2009; Tian et al., 2013). In the present study, we took interest in investigating six PCBs-DL (non-ortho PCBs: PCB-77 and 81; mono-ortho PCBs: PCB-105, 114, 118, and 167) due to their toxicological properties similar to 2,3,7,8-tetrachlorodibenzo- p-dioxin (2378-TCDD) (Kannan et al., 1989; Giesy et al., 1998; Nakata et al., 2003). The highest concentration of  $\sum_6\text{PCBs-DL}$  was detected at Beirut Port reaching 627  $\mu\text{g.kg}^{-1}\text{dw}$  and accounting for 48.1 % of total PCBs and 63.4 % of  $\sum_{12}\text{DL-PCBs}$  (Table 4). The lowest concentration of  $\sum_6\text{PCBs-DL}$  was occurred at Jounieh Bay reaching 13  $\mu\text{g.kg}^{-1}\text{dw}$  and accounting for 9.24 % of total PCBs and 51.1 % of  $\sum_{12}\text{PCBs-DL}$ . The  $\sum_6\text{PCBs-DL}$  is >50 % of  $\sum_{12}\text{PCBs-DL}$  at all investigated stations were represent respectively 95.5, 63.4, 71.8 and 55.5 % at Abou Ali estuary, Beirut Port, Port of Jiyeh power plant and Chekka Bay. Therefore, a high level of concern should be taken consideration for these pollutants during pollution management.

The highest concentration of non-ortho PCB-77 was determined at Port of Jiyeh Power Plant (54  $\mu\text{g.kg}^{-1}\text{dw}$ ). On the other hand, three mono-ortho PCBs congeners (PCB 118, 105 and 167) are dominant for other sampling stations accounting 219  $\mu\text{g.kg}^{-1}\text{dw}$  and 36

$\mu\text{g.kg}^{-1}\text{dw}$  for CB 167 at Abou Ali estuary and Chekka Bay, and  $329 \mu\text{g.kg}^{-1}\text{dw}$  and  $4 \mu\text{g.kg}^{-1}\text{dw}$  for CB 105 at Beirut Port and Jounieh Bay, respectively. Moreover, the quantification and evaluation of potential toxicity of sediment was performed by calculation the total toxic equivalent quantity (TEQ *carc*) (Savinov et al., 2003; Nadal et al., 2004; Qiao et al., 2006; Chen & Chen, 2011) and sediment quality guideline quotient (SQGQ) (Tian et al., 2013). The TEQ *carc* was calculated for all C-PAHs and six PCBs-DL using the following equation (1) (Shen et al., 2010; Tian et al., 2013):

$$TEQ_{carc} = \sum_i C_i \times TEF_i^{carc} \quad (1)$$

where,  $C_i$  is individual C-PAHs or PCBs-DL concentration ( $\mu\text{g.kg}^{-1}\text{dw}$ ); TEF *carc* (toxic equivalency factors) is the toxic factor of carcinogenic PAHs relative to BaP because BaP is the only PAH for which toxicological data are sufficient for derivation of a carcinogenic potency factor (Peters et al., 1999). Whereas, TEFs for BaA, Chr, BbF, BkF, BaP, IP, and DBA are 0.1, 0.001, 0.1, 0.01, 1, 0.1, and 1, respectively, according to the US Environmental Protection Agency (US EPA, 1993). In addition, the World Health Organization (WHO) has developed a suit of TEFs for six PCBs-DL are 0.0001; 0.0003; 0.00003 for PCB 77, PCB 81 and PCB 105, 114, 118 and 167, respectively (Tian et al., 2013). In this study, TEQ PAHs ranged from 59 to  $872 \mu\text{g TEQ.kg}^{-1}\text{dw}$  (Table 4). The maximum value of TEQ PAHs was found at Beirut Port indicating the presence of local sources related to shipping and transport activities occurred in the Port (Sprovieri et al., 2007) causing a great impact on coastal species in this basin. The minimum value was found at Jounieh Bay indicating that touristic activities have a minor contribution of TEQ PAHs due to the dominance of petrogenic PAHs at this station with LMW which are susceptible to the dissolution, biodegradation and desorption processes during transport (Tian et al., 2013). Among C-PAHs, the DBA has a major contribution of TEQ PAHs at Abou Ali estuary, Chekka Bay and Beirut Port accounting for 49.6 %, 49.2 % and 45.4 % respectively. While carcinogenic BaP has a major contribution of TEQ PAHs at Jounieh Bay and Port of Jiyeh Power Plant accounting for 80.9 % and 64.1 % respectively (Fig. 5a). Based on these findings, we suggest that the major contribution of DBA in TEQ PAHs mainly related to the dominance of pyrogenic sources of PAHs in Abou Ali estuary, Chekka Bay and Beirut Port. In contrast, the major contribution of BaP in TEQ PAHs for the remaining stations mainly related to the dominance of petrogenic sources of PAHs. TEQ PCB are ranged from 0.002 to  $0.019 \mu\text{g TEQ.kg}^{-1}\text{dw}$  (Table 4). The highest TEQ PCB was determined also at Beirut Port located in the capital, where

intensive shipping and industrial activities occur in the harbor with a high density population in this city. The non-ortho PCB 81 contributed to highest TEQ PCB at Port of Jiyeh power plant and the mono-ortho PCBs 118 and 105 have a major contribution of TEQ PCB at Beirut Port and CB 167 has a major contribution at Abou Ali estuary (Fig. 5b). However, TEQ PAH and TEQ PCB showed the highest values at of Beirut Port followed by Abou Ali estuary (Table 4) indicating that the largest contribution of TEQ carc in Lebanese coastal sediments came from harbor and/or industrial activities and riverine input. Therefore, during risk assessment and pollution management, more attention should be focused on PAHs and PCBs congeners with high TEQ contributions, rather than only the congeners with high concentrations.

In addition, several tools have been developed to assess the potential biological adverse effects of the sediments at sites affected by contaminant mixtures (Long et al., 1998). The Sediment Quality Guidelines (SQGs) established by US National Oceanic and Atmospheric Administration (NOAA) is widely used to estimate the potential biological adverse effects of PAHs and PCBs contamination in marine and estuarine sediments (Long et al., 1995; Quiroz et al., 2010; Wang et al., 2015), based on two effective approaches designed ERL/ERM values (effects range low and effect range median) developed by Long et al., (1995) and TEL/PEL values (threshold effect level and probable effect level) developed by MacDonald et al., (1996). Three ranges of concentrations are used in the classification of biological adverse effects were expected rarely ( $<ERL/TEL$ ), occasionally ( $\geq ERL/TEL$  and  $<ERM/PEL$ ) and frequently ( $\geq ERM/PEL$ ) (Long et al., 1995; Cardellicchio et al., 2007). According to ERL/ERM values, the biological adverse effects of PAHs can be expected rarely for all stations. The concentrations of  $\sum_{12}PAHs$  were below ERL while these biological adverse effects are rarely expected at Abou Ali estuary, Chekka Bay and Port of Jiyeh power plant and would occur occasionally at Jounieh Bay and Beirut Port according to TEL/PEL values (655/6676  $\mu g.kg^{-1}dw$ ). In contrast, the biological adverse effects of PCBs can be expected frequently for all stations except for Jounieh Bay, which expected to occur occasionally according to the both approaches values ERL/ERM and TEL/PEL.

Furthermore, the mean sediment quality guideline quotient (mSQGq), including mean ERM quotient (mERMq) and mean PEL quotients (mPELq), was applied in this study for deep evaluation of synergic effects of contaminants in sediments (Long & MacDonald, 1997; Long et al., 2006; Cardellicchio et al., 2007) and to obtain a clear picture of the potential biological adverse effect at each station along LCZ. Briefly, mSQGq is

calculated by dividing the individual concentrations of PCBs and 12 PAHs in sediments by their respective ERM and PEL values in SQG then calculating the mean of the quotients for all contaminants at each station following these two equations (Long et al., 1998; Bicego et al., 2006; Cardellicchio et al., 2007):

$$ERMqiorPELqi = \frac{Ci}{ERMiorPELi} \quad (2)$$

$$mERMormPELq = \frac{\sum_{i=1}^n ERMqiorPELqi}{n} \quad (3)$$

where ERM and PEL is the SQG value for the contaminant *i* and *C<sub>i</sub>* is the measured concentration of the same contaminant and *n* is the total number of analysed contaminants (nPAHs = 12 and nPCBs = 28) whose sediment quality guidelines are available.

This SQGq index defines four levels associated to the potential biological adverse effects: highest (mERMq>1.5 and mPELq>2.3), medium-high (mERMq ranged from 0.51 to 1.5; mPELq ranged from 1.51 to 2.3), medium-low (mERMq ranged from 0.11 to 0.5; mPELq ranged from 0.11 to 1.5) and lowest (mERMq<0.11 and mPELq<0.11) (Cardellicchio et al., 2007). Table 4 indicates that the potential biological adverse effect of PAHs and PCBs are ranged from low to medium - low for all investigated stations along LCZ. These results were in agreement with distribution pattern of PAHs and PCBs for all stations indicating that the most polluted sites were strongly influenced by harbor and power plant activities due to the limited water circulation and the open sea exchange in closed basins. Although, the influence of cement factories at Chekka Bay, the effects were considered low for both PAHs and PCBs confirming our hypothesis that long trees and high mountains regions surrounding this bay play as traps for these contaminants, thus reducing their impact on aquatic ecosystem.

This is the first assessment study of organic contamination in surface sediments of the Lebanese coast. This work has provided data on the levels of PAHs, Me-PAHs and PCBs in sediments of several hotspots zones located along LCZ extending from the north to south Lebanon including Abou Ali estuary, Chekka and Jounieh Bay, Beirut and Jiyeh Port. The highest contamination of PAHs, Me-PAHs and PCBs were found at Beirut Port located in densely populated area and subjected to multidisciplinary activities including industrial inputs, intensive shipping and transport activities. This indicate a strong influence of the anthropogenic activities on the level of PAHs and PCBs in coastal sediments. The significant contamination is not only related to the vicinity of the most probable sources of pollution, but also in area of intensive sedimentation and limited

water circulation. High mountain regions play as traps to these contaminants by reducing their fate in coastal sediments such as the case at Chekka bay where we observed clearly that the impact of cement factories and harbor activities are limited. According to Baumard et al. (1998a), the classification of PAHs pollution levels could be considered as moderate for all sampling sites except for Beirut Port which is highly polluted with PAHs. The composition profile study of pollutants provides a valuable information in source identification where the results show the abundance of PAHs with MMW and HMW at Abou Ali estuary, Chekka Bay and Beirut Port sediments while PAHs with LMW are greater represented at Jounieh Bay and Jiyeh power plant. The use of different diagnostic ratios gives an inconsistent picture of PAHs origins and seem to be inadequate for the differentiation of hydrocarbon origins. Only the ratio (LMW/HMW) can be considered a reliable tool for discriminating between petrogenic and pyrogenic origins of PAHs in our study confirming that pyrogenic processes were the predominance source of PAHs at Abou Ali estuary, Chekka Bay and Beirut Port characterized by the abundance of PAHs with MMW and HMW, while the petrogenic was the predominance source at Jounieh Bay and Port of Jiyeh power plant characterized by the abundance of PAHs with LMW. For PCBs, LCZ is polluted by higher chlorinated congeners characterized by the abundance of Medium to High chlorinated PCBs with the content varying from 4 to 9 chlorine atoms. No diagnostic ratios of PCBs congeners can be found in the literature. The source identification of PCBs based upon an interpretive analysis method of literature results and composition profile congeners suggesting that atmospheric deposition is a primarily source of PCBs emissions in urban and industrial regions along LCZ. The evaluation of potential toxicity of PAHs and PCBs-DL was performed based on the calculation of TEQ<sub>carc</sub> of C-PAHs and six PCBs-DL and SQG<sub>q</sub>. TEQ<sub>PAHs</sub> and TEQ<sub>PCBs</sub> suggest a relatively elevated level of toxicity at Beirut Port followed by Abou Ali estuary indicating that the largest contribution of TEQ<sub>carc</sub> in Lebanese coastal sediments came from harbor, industrial activities and riverine input. During risk assessment and pollution management great concerns should be taken to PAHs and PCBs congeners with high TEQ contributions, rather than the congeners with high concentrations. The potential biological adverse effect of PAHs and PCBs are ranged from low to medium - low for all investigated stations along LCZ according to SQG<sub>q</sub>. This paper provides a single approach for PAHs and PCBs contamination assessment along LCZ including distribution of concentration pattern, composition profile, sources identification and toxicity risk assessment. The gathered data in this

study should be used as a baseline reference concentration and risk assessment by policy and decision makers as part of a program of integrated coastal zone management on biodiversity, sediment–water quality and economic activities along LCZ in particular during future activities in gas and oil sector. A detailed study at Beirut Port is recommended to describe deeply the potential sources and take efficient control measures of the inputs in order to improve the quality of sediments and marine environment. Further studies for other potential contaminants (i.e., heavy metals, pesticides, TBT and PCDD/Fs) also recommended to achieve the knowledge on persistent toxic pollutants along LCZ located in the eastern basin of Mediterranean Sea.

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Table 1: Factor loading from Principal Component Analysis with equamax rotation

	Component		
	1	2	3
pH	.071	.816	.100
Eh	-.170	-.461	.716
Sand	-.561	-.677	.151
Silt	.669	.428	-.044
Clay	.442	.724	-.187
TOC	.262	.897	-.172
TN	.250	.892	.015
TS	.183	.677	-.291
Cd	.259	.218	.812
Co	.889	.237	.017
Cu	.582	.734	-.082
Fe	.885	.309	.145
Mn	.675	-.269	.538
Ni	.888	.148	.133
Pb	.702	.366	.272
Zn	.775	.546	-.151

**Table 1:** Description of the five investigated sampling sites along LCZ.

Site name	Stations	Coordinates	Depth (m)	Description	
Jiyeh Port	SPJ1	33°38'53.85"N 35°23'53.50"E	4	Commercial Harbor	Shipping activities essentially reserved to the fuel supply for the Power plant
	SPJ2	33°38'53.85"N 35°23'53.50"E	6		
	SPJ3	33°38'53.85"N 35°23'53.50"E	10		
Beirut Port	SPB1	33°54'18"N 35°31'16"E	2	Commercial Harbor	Loading/unloading of general cargos, container operations, and shipping, transportation and fishery activities with the presence of three industrial buildings.
	SPB2	33°54'18"N 35°31'16"E	3		
	SPB3	33°54'18"N 35°31'16"E	5		
Jounieh bay	SJB1	33° 58' 59"N 35°38' 59" E	4	Touristic beach resort (marina)	Touristic activities including swimming, water sports, boating and fishing and yachting center.
	SJB2	33° 58' 59"N 35°38' 59" E	6		
	SJB3	33° 58' 59"N 35°38' 59" E	10		
Chekka bay	SCB1	34°20'4.01"N 35°43'25.75"E	3	Touristic beach resort (marina)	Touristic activities and the presence of two cement factories located about hundred meters away from this beach.
	SCB2	34°20'4.01"N 35°43'25.75"E	4		
	SCB3	34°20'4.01"N 35°43'25.75"E	7		
Abou Ali estuary	SAE1	34°27'30.16"N 35°50'29.68"E	3	Estuary	Coastal sea receives approximately 369 mm <sup>3</sup> /year freshwater input from Abou Ali River which is highly affected by anthropogenic activities.
	SAE2	34°27'30.16"N 35°50'29.68"E	6		
	SAE3	34°27'30.16"N 35°50'29.68"E	9		

**Table 2:**

List of targeted compounds and Mean of Individual concentration of PCBs, PAHs and Me-PAHs in  $\mu\text{g.kg}^{-1}$  dw for sediment samples collected from five sample stations along LCZ (mean of three determinations) with the total mean values at each station.

<i>Compounds</i>	<b>16 PAHs</b>				
	<b>Abou Ali stuary</b>	<b>Chekka Bay</b>	<b>Jounieh Bay</b>	<b>Port of Beirut</b>	<b>Port of Jiyeh</b>
<i>Nap</i>	11.9	12.9	231.8	225.6	72.9
<i>Acy</i>	3.1	2.8	0.9	36.7	50.2
<i>Ace</i>	10.9	3.9	13.1	40.7	54.5
<i>Fl</i>	5.9	42.4	11.5	48.9	39.3
<i>Phe</i>	43.1	56.3	334.5	65.9	79.9
<i>Ant</i>	8.1	2.7	141.2	169.3	71.3
<i>Pyr</i>	22.6	13.9	11.3	59.9	2.3
<i>Flu</i>	35.4	19.2	8.5	390.9	32.0
<i>BaA</i>	12.1	1.4	ND	519.3	17.8
<i>Chr</i>	13.4	3.9	2.3	165.4	20.2
<i>BbF</i>	60.9	38.2	24.6	466.7	7.8
<i>BkF</i>	118.9	70.8	91.7	302.5	39.3
<i>BaP</i>	69.5	34.1	47.4	358.1	10.6
<i>IP</i>	98.4	80.8	78.2	161.6	29.5
<i>DBA</i>	86.6	45.3	ND	396.3	ND
<i>BgP</i>	67.0	108.7	ND	364.7	24.7
$\Sigma_{16}$ HAPs	667.8	537.1	997.1	3772.6	552.4
			<b>18 Me-PAHs</b>		
<i>1-methylnaphthalene</i>	7.1	35.1	14.5	130.9	19.3
<i>2-methylnaphthalene</i>	7.8	45.5	15.1	72.8	24.3
<i>1,2-dimethylnaphthalene</i>	15.1	107.2	36.2	306.0	67.4
<i>1,6-dimethylnaphthalene</i>	13.0	77.8	31.4	232.9	52.9
<i>2,6-dimethylnaphthalene</i>	12.2	57.9	59.9	121.7	58.3
<i>1-methylphenanthrene</i>	8.1	3.9	0.9	648.6	11.6
<i>2-methylphenanthrene</i>	10.6	3.3	1.1	1164.9	14.4
<i>3-methylphenanthrene</i>	8.2	3.4	1.3	3913.1	44.5
<i>9-methylphenanthrene</i>	12.7	3.1	0.9	1339.8	51.3
<i>2-methylanthracene</i>	10.2	2.6	0.8	714.5	16.3
<i>1,7-dimethylphenanthrene</i>	22.1	8.2	3.1	1999.4	77.8
<i>Retene</i>	31.7	10.8	7.4	ND	41.6
<i>1-methylfluoranthene</i>	15.5	2.9	1.8	116.2	10.0
<i>3-methylfluoranthene</i>	14.7	3.5	1.9	148.4	9.9
<i>1-methylpyrene</i>	13.6	2.4	1.7	207.7	77.5
<i>4-methylpyrene</i>	9.2	3.6	1.8	215.5	62.4
<i>3-methylchrysene</i>	20.2	1.6	3.4	ND	44.1

6-methylchrysene	18.9	2.9	3.9	208.6	47.7
$\Sigma_{18}$ Me-PAHs	250.8	375.7	187.2	11541.1	731.2

**28 PCBs**

<i>Compounds</i>	<b>Abou Ali stuary</b>	<b>Chekka Bay</b>	<b>Jounieh Bay</b>	<b>Port of Beirut</b>	<b>Port of Jiyeh</b>
CB8	ND	ND	ND	ND	ND
CB18	ND	ND	ND	ND	ND
CB28	5.2	2.99	4.4	172	33.4
CB52	7.5	ND	ND	ND	102.0
CB44	ND	ND	ND	ND	ND
CB66	3.4	1.65	2.7	ND	33.1
CB101	6.6	1.53	ND	ND	59.6
CB81	ND	3.17	2.7	ND	26.9
CB77	ND	ND	2.6	ND	53.8
CB123	ND	ND	2.7	103.7	46.9
CB118	ND	ND	2.5	297.5	38.7
CB114	45.8	ND	1.7	ND	ND
CB153	3.9	0.46	1.1	64.3	16.9
CB105	ND	ND	3.6	329.3	0.0
CB138	10.4	2.92	2.9	22.8	71.0
CB126	8.6	ND	2.6	83.9	ND
CB170	ND	6.81	ND	ND	26.9
CB128	ND	ND	ND	ND	72.5
CB157	ND	ND	ND	ND	ND
CB156	ND	ND	3.7	119.4	ND
CB169	ND	ND	3.8	55.1	ND
CB180	3.6	ND	ND	18.2	51.3
CB167	218.6	35.97	ND	ND	ND
CB187	ND	18.06	ND	ND	85.3
CB189	3.9	31.35	ND	ND	ND
CB195	ND	42.42	49.6	ND	ND
CB206	21.9	103.30	56.1	37.1	ND
CB209	ND	ND	ND	ND	ND
$\Sigma_{28}$ PCBs	339.4	250.63	142.6	1303	718.2

\* ND: not detected

**Table 3:**

(A) Characteristic values and (B) source identification based on selected molecular, isomeric and homologue alkyl PAHs ratios for petrogenic and pyrogenic origins of PAHs for sediment samples collected from five sampling stations along LCZ.

(A) Ratios	Petrogenic	Mixed sources	Pyrogenic	Abou Ali estuary	Chekka Bay	Jounieh Bay	Port of Beirut	Port of Jiyeh	References
LMW/HMW	>1	-	<1	0.14	0.29	2.78	0.18	2.00	Sicre et al., 1987 Budzinski et al., 1997
BaA/ (BaA+Chr)	<0.2	0.2-0.35	>0.35	0.47	0.26	0.00	0.76	0.47	Yunker et al. 2002
IP/ IP+BghiP	<0.2	0.2-0.5	>0.5	0.59	0.43	1.00	0.31	0.54	Wang et al., 1999 Yunker et al. 2002
Flu/Pyr	<1	-	>1	1.57	1.38	0.75	6.53	13.93	Baumard et al., 1998a, b De Luca et al., 2005
C0 / (C0+C1) F/P	<0.5	-	>0.5	0.52	0.73	0.74	0.40	0.18	Yunker et al. 2002, 2012

(B) Ratios	Abou Ali estuary	Chekka Bay	Jounieh Bay	Port of Beirut	Port of Jiyeh
LMW/HMW	Combustion	Combustion	Petroleum	Combustion	Petroleum
BaA/ (BaA+Chr)	Combustion	Mixed sources	Petroleum	Combustion	Combustion
IP/ IP+BghiP	Combustion	Mixed sources	Combustion	Mixed sources	Combustion
Flu/Pyr	Combustion	Combustion	Petroleum	Combustion	Combustion
C0 / (C0+C1) F/P	Combustion	Combustion	Combustion	Petroleum	Petroleum

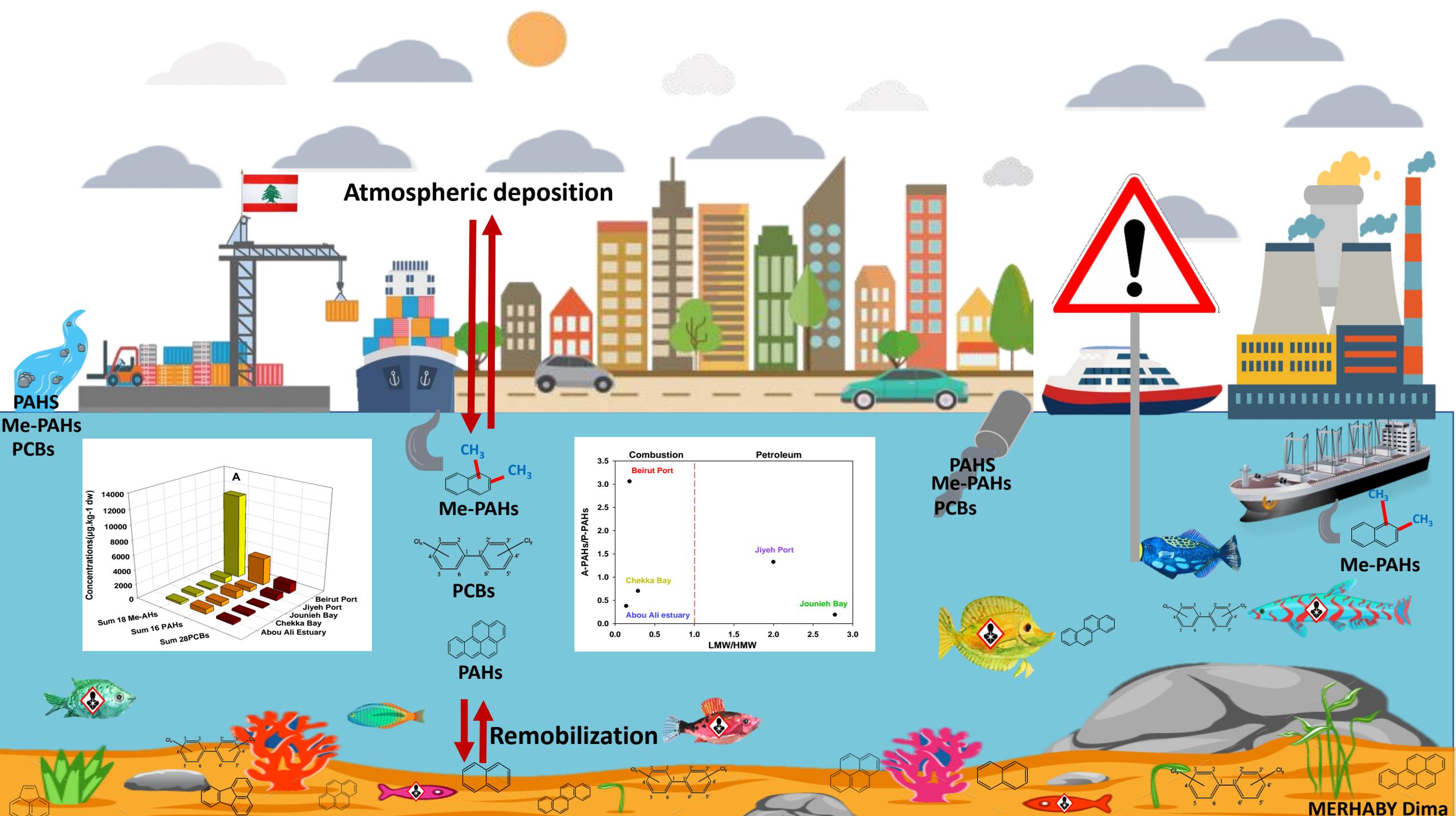
LMW/HMW: sum of (Naph, Ace, Acy, Fl, Ph and Anth) concentrations against sum of (Flu, Pyr, BaA, Chr, BbF, BkF, BaP, IP, DBA and BgP) concentrations. BaA/(BaA+Chr): concentration of BaA against sum of concentrations of BaA and Chrysene. IP/ IP+BghiP: concentration of IP against sum of concentrations of IP and BgP. Flu/Pyr: Concentration of Flu against concentration of Pyr. .

**Table 4:**

C-PAHs, sum of six PCBs-DL, sum of 12 PAHs, TEQ<sub>PAH</sub>, TEQ<sub>PCB</sub>, SQGQ<sub>PAH</sub> and SQGQ<sub>PCB</sub> for all sampling stations along LCZ.

<b>Sampling stations</b>	<b>C-PAHs</b> ( $\mu\text{g.kg}^{-1}\text{ dw}$ )	<b><math>\Sigma 6</math> PCBs- DL</b> ( $\mu\text{g.kg}^{-1}\text{ dw}$ )	<b><math>\Sigma 12</math>-PAHs</b> ( $\mu\text{g.kg}^{-1}\text{ dw}$ )	<b>TEQ<sub>PAH</sub></b> ( $\mu\text{g TEQ.kg}^{-1}\text{ dw}$ )	<b>TEQ<sub>PCB</sub></b> ( $\mu\text{g TEQ.kg}^{-1}\text{ dw}$ )	<b>m ERMq PAHs</b>	<b>mPELq PAH</b>	<b>PAHs effects</b>	<b>mERMq PCBs</b>	<b>mPELq PCBs</b>	<b>PCBs Effects</b>
<i>Abou Ali Estuary</i>	460	264	323	174	0.008	0.04	0.09	low	0.07	0.06	low
<i>Chekka Bay</i>	274	39	239	92	0.002	0.03	0.08	low	0.05	0.05	low
<i>Jouniyeh Bay</i>	244	13	803	59	0.001	0.05	0.17	Medium - low	0.03	0.03	low
<i>Beirut Port</i>	2370	627	2477	872	0.019	0.23	0.59	Medium - low	0.26	0.25	Medium - low
<i>Jiyeh Port</i>	125	119	451	17	0.015	0.04	0.17	Medium - low	0.14	0.14	Medium - low

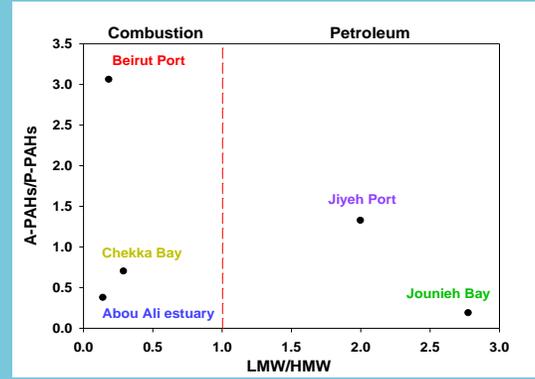
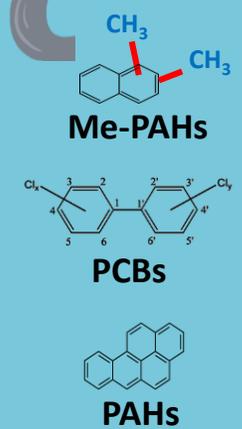
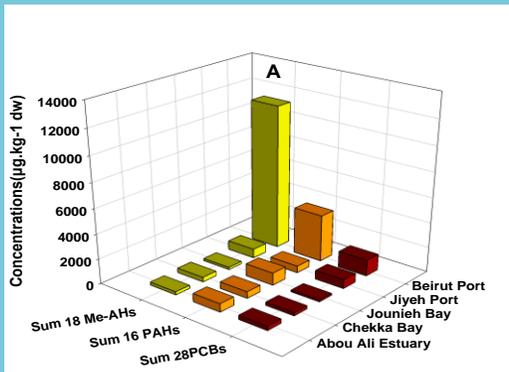
Total concentration of potentially carcinogenic PAHs (C-PAHs; BaA, Chr, BaP, BbF, BkF, IP, and DBA). Six PCBs-DL (non-ortho PCBs: PCB-77 and 81; mono-ortho PCBs: PCB- 105, 114, 118, and 167). Total toxic equivalent quantity (TEQ<sub>carc</sub>) and sediment quality guideline quotient (SQG<sub>Q</sub>). ERL/ERM values (effects range low and effect range median) (PAHs: 4022/44792  $\mu\text{g.kg}^{-1}\text{ dw}$ /PCBs: 23/180  $\mu\text{g.kg}^{-1}\text{ dw}$ ). TEL/PEL values (threshold effect level and probable effect level) (PAHs: 655/6676  $\mu\text{g.kg}^{-1}\text{ dw}$ /PCBs: 22/189  $\mu\text{g.kg}^{-1}\text{ dw}$ ).



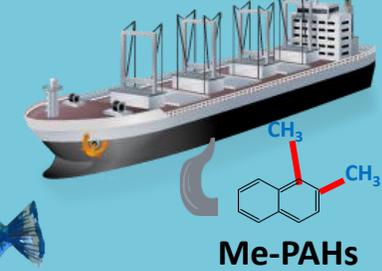
## Atmospheric deposition



PAHS  
Me-PAHs  
PCBs



PAHS  
Me-PAHs  
PCBs



## Remobilization

