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Organic pollution in surficial sediments of Tripoli harbour, Lebanon

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ABSTRACT

Tripoli harbour is among the most important ports on the Mediterranean Sea eastern basin. The persistent organic pollutants (POPs) were monitored (28 PCBs, 16 PAHs and 18 Me-PAHs) in 15 stations of Tripoli harbour basins, which are influenced by anthropogenic activities. Total PAHs concentrations ranged from 243 to 2965 $\mu\text{g kg}^{-1}$ dw, total Me-PAH concentrations ranged from 54 to 1638 $\mu\text{g kg}^{-1}$ dw, while total PCB levels ranged from 18 to 302 $\mu\text{g kg}^{-1}$ dw. PCBs profiles were dominated by four and six-chlorinated congeners while the PAHs were dominated by four and five rings. For identifying pollution emission sources of PAHs, different ratios were used. The results show that the pollution origin was predominated by pyrogenic process related to the deposition of coal dust and the combustion of biomass and coal. Based on Sediments Quality Guidelines the biological adverse effects on aquatic ecosystems were expected rarely to occasionally for PAHs and PCBs contamination.

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The coastal areas play an important role in the economic and social development at the local, national and global scales. However, the excessive exploitation of these areas can cause a significant threat to marine environment. Coastal area usually act as receptors for several types of discharges and dumping wastes containing high levels of persistent organic pollutants (POPs) generated from anthropogenic activities (Zhou et al., 2000). Various families of POPs were found in environmental media. Among the principal classes, there are the aromatics compounds, including parent and alkyl-substituted polycyclic aromatic hydrocarbons (PAHs and Me-PAHs) and polychlorinated biphenyls (PCBs). Due to their physicochemical properties, their ubiquitous, their persistence, their transportability, and fat-solubility (Jones and Voogt, 1999), these compounds tend to bioaccumulate in fatty tissue and have potential adverse effects on aquatic ecosystems and human health via food chains (Jones and Voogt, 1999; Fleeger et al., 2003; Manodori et al., 2006; Fernández et al., 2012). Moreover, these contaminants are known or suspected as mutagenic and carcinogenic (Jones and Voogt, 1999; Qiao et al., 2006; Chen et al., 2012) and their endocrine disrupting activities in humans and wildlife have been recently reported for PAHs and PCBs (Clemons et al., 1998; Jones and Voogt, 1999; Brun et al., 2004).

PAHs and Me-PAHs are widely spread chemical pollutants released into the environment. They can be originated either from natural processes including biomass burning, volcanic eruptions

and diagenesis (Wang et al., 2007), and from anthropogenic inputs such as fuels or oil spills and their incomplete combustion. Anthropogenic origins are generally the major sources of PAHs pollution in the environment (Chen et al., 2013; Acquavita et al., 2014; Mirza et al., 2014). PAHs can enter water surface as a mixture origin via atmospheric deposition, water run-off, municipal and industrial effluents, sewage outfalls, oil spillage and maritime transport (Maher and Aislabie, 1992; Manoli and Samara, 1999; Zhou and Maskaoui, 2003). In the case of sediment resuspension, some PAHs in water could adsorb on the sediment particles and flocculate, leading to an accumulation of PAHs in sediment (Feng et al., 2012). Due to their mutagenic and carcinogenic properties, 16 PAHs are listed as priority pollutants by the US Environmental Protection Agency (USEPA) (Keith and Telliard, 1979; Conney, 1982; Connel et al., 1997; Straif et al., 2005; Cardellicchio et al., 2007; IARC, 2010; Tobiszewski and Namiesnik, 2012). The emission sources of hydrocarbons can be determined using different diagnostic ratios (Tobiszewski and Namiesnik, 2012; Yunker et al., 2002).

Since 1930s, PCBs have been used as insulating fluids in electronic equipment and additives in paints and rubbers sealants. Industries contributed for a large amount of PCBs into environment (Harrison, 2001; Cardellicchio et al., 2007; Fernández et al., 2012). PCBs in environment can be originated from improper disposal, leakage, atmospheric deposition (e.g. incineration and volatilization) (Smedes and de Boer, 1997; Cardellicchio et al., 2007; Fernández et al., 2012). Anthropogenic pollutions particularly from shipping and industrial activities are responsible of PCBs in the

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environment (Hong et al., 2005, 2006). However, little are known about PCBs pollution but PCBs still a major concern due to the multiplicity of sources and transport mechanisms (Hutzinger et al., 1974; Atlas et al., 1986; Lakshmanana et al., 2010; Fernández et al., 2012). Therefore, due to their strong stability under environmental conditions, PCBs are also listed in priority organic pollutants (WHO, 1993; Cardellicchio et al., 2007).

PAHs and PCBs are characterized by their hydrophobic properties which allow their adsorbing with suspended particulate matter (SPM) and finally deposited in the sediment which constitutes a reservoir (Glynn et al., 1995; Tkalin, 1996; Zhou et al., 1996, 1998, 2000; Manoli and Samara, 1999; Jones and Voogt, 1999; Nemr and Abd-Allah, 2003; Page et al., 1999). Contaminated sediments become an important source of pollution and can pose significant threat to aquatic organisms and humans health (Wernersson et al., 2000; Del Valls et al., 2004), particularly when sediments are disturbed or dredged. High bioavailability of PCBs occurred frequently in harbour areas due to the intensive shipping and dredging activities (Eggleton and Thomas, 2004; Nikolaou et al., 2009). Indeed, harbours are critical areas where can concentrate and release a large amount of POPs into environment, due to intensive shipping activities and maritime transport. The ports are very complex systems, influenced strongly by anthropogenic activities. These include urban, surrounding industrial activities or installations that do not necessarily belong to the port (Darbra et al., 2004; Ruggieri et al., 2011). However, recent studies about organic contamination are concentrated only on the north-western part of the Mediterranean Sea (Lipiatou et al., 1997; Dachs et al., 1999) and there are great lacks of information on the Eastern part (Gogou et al., 2000).

Hence, there is an urgent need to assess the organic contamination for the whole of the Mediterranean Sea (Nikolaou et al., 2009). The objective of this paper is to assess the spatial distribution pattern of 16 PAHs, 18 Me-PAHs and 28 PCBs in surface sediment in Tripoli harbour (Eastern Mediterranean Sea, Northern Lebanon) in order to identify their emission sources and thus their potential ecotoxicological effects by comparison with sediment quality guidelines levels (SQGs). The determination of these contaminants has been performed using accelerated solvent extraction (ASE), followed by conventional liquid column chromatography (silica column) for purification and separation. Finally, the extracts are analysed by gas chromatography coupled to mass spectrometry (GC-MS).

Sediments 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). 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). Tetrachloronaphthalene (TCN), 2,3,3',5,6-tetrachlorobiphenyl (PCB112) and octachloronaphthalene (OCN), used for PCB quantification, were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Deuterated internal standards for PAHs and Me-PAHs (acenaphthene-*d*10 (A-*d*10), naphthalene-*d*8 (N-*d*10), perylene-*d*12 (Per-*d*12), phenanthrene-*d*10 (Phe-*d*10) and pyrene-*d*10 (Pyr-*d*10)) were provided by LGC-Promochem (Middlesex, UK). HPLC-grade solvents (hexane, dichloromethane, methanol and acetone) were purchased from Dislab (France). No significant amount of targeted analytes was showed in procedural blanks. Ultrapure water (Milli-Q) was produced by a Millipore apparatus with 18.2 MΩ cm⁻¹ resistivity. Merck silica gel 60 (70–230 mesh ASTM) activated at 450 °C was heated at 120 °C for 12 h 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.

For the past several hundred years, Tripoli City (North Lebanon) has been serving as important seaports for shipping, transportation

and fishery activities. Port of Tripoli located in the Northern area of Tripoli city (34°27'19"N, 35°49'14"E) is the second port in Lebanon after the Port of Beirut. It is among the most important port on the eastern basin of the Mediterranean Sea because it is a link between East and West. The port covers an area of approximately 3 million m², with a water area of 1,500,000 m², and a land area that consists of 950,000 m², and a 550,000 m² of dump area destined as a future free economic zone. Indeed, Tripoli Port is divided into two ports; the first one for the harbour activities and the second for fishery activities. Harbour has 2 semi-enclosed basins due to the presence of two breakwaters 1900 m and 1300 m long respectively and 1000 m with depths varying from 8 to 10 m for operated old quay and 1200 m long with 15.2 m depth for the new quay. The old quay receives general cargos and dry Bulk such as steel, wood, sugar, various kinds of beans, iron scrap, vehicles, construction material, fertilizers and coal. The new quay will be used for multi-purpose terminal; 400 m long specialized in the handling of containers ships and the others 200 m specialized in the service of big dry bulk ships. Actually, the harbour receives about 450 ships par year.

Tripoli harbour was chosen because it is influenced by multiple anthropogenic activities, which can contribute to the introduction of PAHs and PCBs into bays and such as harbour facilities (e.g. Shipping and transport operations, storm water runoff and dredged materials), urbanization (e.g. Sewage outfall, landfill lixivate) and commercial fishing. Also, the location of the harbour 80 km away from the capital Beirut and only 30 km from the border with Syria contributes in a very important transit activity, which can be source of pollution via atmospheric deposition. Moreover, Tripoli harbour is considered as a critical area due to the presence of natural reserves (Palm, Sanani and Rabbit Island) at 5.5 km far from the coastal which can face important pressure from contaminants associated with ports activities and thus, can cause environmental and ecological effects on marine ecosystem.

In fact, no data are available about the organic contamination in this area and our study is the first. 15 sediment samples were collected from three semi-enclosed basins in Tripoli harbour (Mediterranean Sea, Northern Lebanon). The sampling sites are presented in Fig. 1. These sampling sites have a scarce water circulation and strongly influenced by harbour, fishery and municipal activities and their characteristics are presented in Table 1.

Sediments were collected in December 2013 at harbour Basins (Fig. 1). Superficial sediments samples (0–5 cm) were collected by diver using glasses tubes properly disinfected. Each sample was homogenized before being transferred into pre-calcinated aluminium containers capped with aluminium foils. Sediment samples were transported in the laboratory and were frozen at –20 °C then dried at room temperature in a laminar hood.

Sediments samples were analysed for 16 PAHs, 18 Me-PAHs and 28 PCBs including 12 dioxin-like PCBs (PCB-DL) and the 7 indicators PCB (PCBi). Targeted compounds were listed below:

PCBs No. (28 PCBs): 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209.

PAHs (16 PAHs): Naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phen), anthracene (Anthr), pyrene (Pyr), fluoranthene (Fluo), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP), indeno[1,2,3-cd]pyrene (IDP).

Me-PAHs (18 Me-PAHs): 1-methylnaphthalene (1-MeNaph), 2-methylnaphthalene (2-MeNaph), 1,2-dimethylnaphthalene (1,2-DMNaph), 1,6-dimethylnaphthalene (1,6-DMNaph), 2,6-dimethylnaphthalene (2,6-DMNaph), 1-methylphenanthrene (1-MePhe), 2-methylphenanthrene (2-MePhe), 3-methylphenanthrene (3-MePhe),

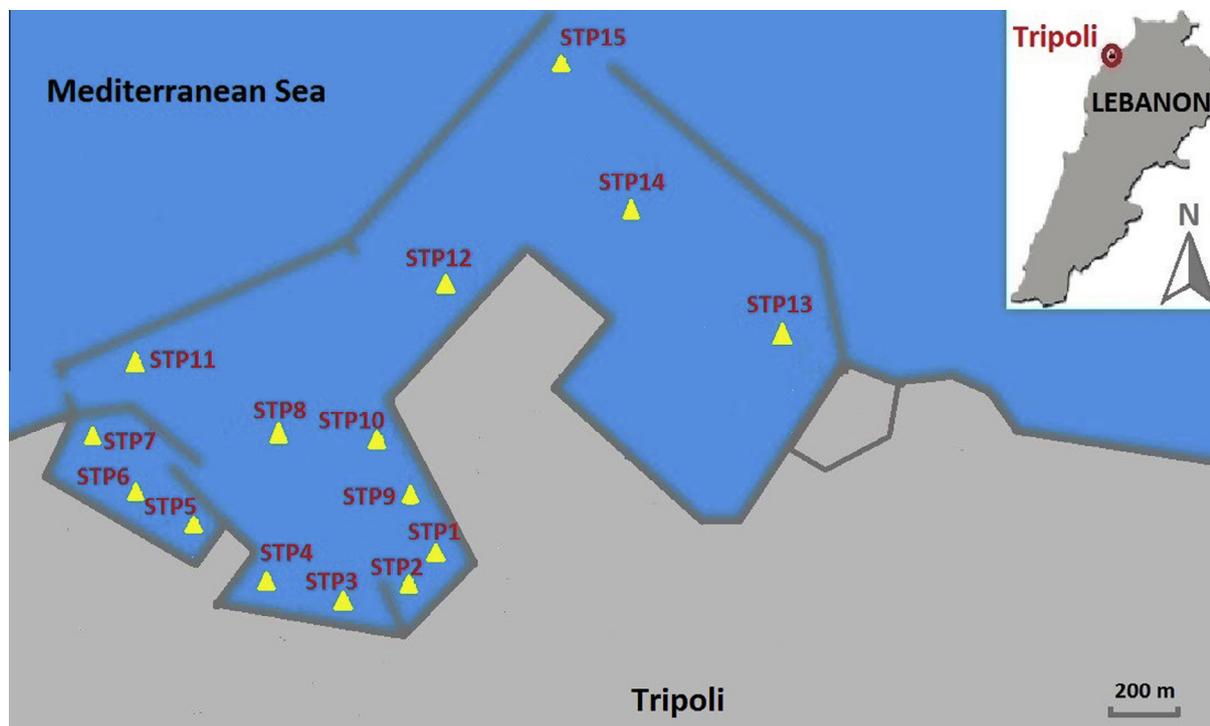


Fig. 1. Location of sampling sites in Tripoli harbour basins, Lebanon. STP: Sediment Tripoli Port. STP1 sample collected from the corner of old basin, STP2 sample collected from old basin close to ships maintenance, STP3 sample collected from old basin close to sewage outfall, STP4 sample collected from old basin close to ships maintenance, STP5, STP6, STP7 samples collected from fishery basin, STP8 sample collected from the mid of old basin, STP9, STP10 samples collected from old basin near the activities of loading/unloading of cargos, STP11 sample collected from old basin before the breakwater, STP12 sample collected from new basin, STP13 sample collected from new basin near to landfill, STP14 sample collected from between new basin and landfill, STP15 sample collected from the entrance of ships.

Table 1
Description of sampling sites in Tripoli harbour basins.

Sites	Latitude	Longitude	Depth (m)	Description
SPT1	34°27'9.42"N	35°49'35.79"E	8	Old basin Corner loading/unloading of scraps and touristic vessels.
SPT2	34°27'7.59"N	35°49'30.96"E	8	Old basin Ships maintenance
SPT3	34°27'5.61"N	35°49'22.72"E	2.5	Old basin Sewage outfall
SPT4	34°27'6.09"N	35°49'12.36"E	2.5	Old basin Ships maintenance
SPT5	34°27'12.26"N	35°49'5.49"E	1.8	Fishery Port Fishery activities
SPT6	34°27'15.66"N	35°48'56.75"E	2	Fishery Port Fishery activities
SPT7	34°27'22.85"N	35°48'52.74"E	1.8	Fishery Port Fishery activities
SPT8	34°27'20.67"N	35°49'18.24"E	6	Old basin/fishery port Mid of old basin and the entrance of fishery port
SPT9	34°27'15.53"N	35°49'31.50"E	8	Old basin Loading/unloading of cargos
SPT10	34°27'20.59"N	35°49'28.53"E	9.5	Old basin Loading/unloading of cargos
SPT11	34°27'29.62"N	35°48'58.36"E	6	Old basin Before breakwater
SPT12	34°27'35.09"N	35°49'35.19"E	15	New basin Future basin for container trade
SPT13	34°27'28.96"N	35°50'18.56"E	16	New basin Near landfill
SPT14	34°27'45.37"N	35°50'0.86"E	16	New basin Between new basin and landfill
SPT15	34°28'0.08"N	35°49'49.64"E	16	New basin Entrance of ships

9-methylphenanthrene (9-MePhe), 2-methylanthracene (2-MeAnthr), 1,7-dimethylphenanthrene (1,7-DMPhe), retene, 1-methylfluoranthene (1-MeFluo), 3-methylfluoranthene (3-MeFluo), 1-methylpyrene (1-MePyr), 4-methylpyrene (4-MePyr), 3-methylchrysene (3-MeChry), 6-methylchrysene (6-MeChry).

Sediment samples were dried under hood, then finely ground and sieved at 224 μm . Approximately 15 g of sieved sediment samples were spiked with internal standards A-d10, N-d10, Per-d12, Phe-d10 and Pyr-d10 for PAHs and Me-PAHs and TCN, PCB112 and OCN for PCBs quantification. After a delay of equilibration, sediments were then extracted using an accelerated solvent extraction

(ASE 200, Dionex Corp., USA). The ASE conditions under which the extraction is carried out were described in [Tronczynski et al. \(2005\)](#). Briefly, the extraction conditions were heat 5 min, temperature 100 °C, static solvent extraction time 2 min with 5 static cycles and two times, pressure 138 bars, purge 3 min and 35% flush and high purity nitrogen was employed as the purge gas.

After the extraction with ASE, molecular sulfur was removed by addition of activated metallic copper to the extracts. The extracts were concentrated, solvent-exchanged to hexane, and were then purified and fractionated by liquid chromatography on a silica column to eliminate organic interferences ([De Boer and Law, 2003](#);

Jeanneau et al., 2007). Targeted compounds were recovered by elution with 15 ml of hexane/dichloromethane mixtures (3/1 v/v) and then 10 ml of hexane/dichloromethane mixture (1/1 v/v) (Fraction 2). Each fraction was concentrated using a rotary evaporator followed by a slight stream of nitrogen.

PAHs, Me-PAHs and PCBs were analyzed 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 μm film thickness) and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS). The carrier gas was helium held at a constant flow rate of 1 mL/min. Each group of organic compounds was analyzed separately. Temperature of the GC oven was programmed as follows: from 70 °C (1 min) to 170 °C at 10 °C/min, then to 230 °C at 4 °C/min, and then to 300 °C at 3 °C/min (13 min) for HAPs and Me-HAPs and from 80 °C (1 min) to 170 °C at 10 °C/min, then to 230 °C at 4 °C/min, and then to 300 °C at 3 °C/min (19 min) for PCBs. Samples were injected in the splitless mode at 280 °C and the injector was purged with helium after 1 min. Identification of each PAH, Me-PAH and PCB was done on the basis of the retention time and the mass spectrum from chromatogram of standard solutions acquired in full scan mode. Quantification was then performed in MS–MS mode for better selectivity. Response factors were determined relative to the internal standards response and to standard mixtures. The individual concentrations of PAHs, Me-PAHs and PCBs were calculated to give the total concentration of each studied contaminants in $\mu\text{g kg}^{-1}$ of dry weight of sediment.

Individual concentration of targeted PCB, PAH and Me-PAH in sediment samples collected from 15 stations of Port of Tripoli basins are presented in Table 2.

Total concentration of PAHs or $\sum_{16}\text{PAHs}$ in sediment samples collected from Port of Tripoli basins ranged from 243 to 2965 $\mu\text{g kg}^{-1}$ dw, with average value of 1061 $\mu\text{g kg}^{-1}$ dw. The highest concentration of 16 PAHs was observed at station STP6 collected from fishery basin with concentration ($\sum_{16}\text{PAHs}$) reaching 2965 $\mu\text{g kg}^{-1}$ dw sediment (Fig. 2). Highest concentrations were observed in STP1, STP3 and STP4 with $\sum_{16}\text{PAHs}$ reaching 2727, 1641 and 1964 $\mu\text{g kg}^{-1}$ dw respectively. Large variation of concentration was observed. This variation indicates the influence of Tripoli basins by multiple sources of PAHs may be produced by fishery activities (STP5 and STP6), harbour activities such as ship maintenance (STP4) and urban discharges (STP3). Low $\sum_{16}\text{PAHs}$ were detected at 243 $\mu\text{g kg}^{-1}$ dw, at STP13 closed to landfill.

Concerning the substituted PAHs, the total concentration of $\sum_{18}\text{Me-PAHs}$ in sediment samples varied between 54 and 1639 $\mu\text{g kg}^{-1}$ dw, with average value 498 $\mu\text{g kg}^{-1}$ dw. The highest concentration was found at STP4 located closed to ship maintenance area with concentration reached 1639 $\mu\text{g kg}^{-1}$ dw. Lower concentration was detected at STP14 collected from the mid of new basin between ship entrance/exit and landfill with concentration 54.2 $\mu\text{g kg}^{-1}$ dw. Concentration increase from STP15 (collected from new basin entrance/exit of ships close) to open sea reached 279 $\mu\text{g kg}^{-1}$ dw. Highest concentrations of $\sum_{18}\text{Me-PAHs}$ detected in STP1, STP2, STP4, STP6 and STP10 with concentrations reached 725, 726, 614, 1638 and 649 $\mu\text{g kg}^{-1}$ dw respectively (Fig. 2) indicate that Me-PAHs contamination of old basin of harbour and fishery basin could be originated from oil spills accidents during ships maintenance and oil leakage during oil supply for fishery boats.

Amongst 28 PCBs studied, 24 PCBs congeners (PCBs 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 157, 169, 170, 180, 187, 206, and 209) were detected and quantified in superficial sediments samples collected from Port of Tripoli basins. Among these 24 PCBs listed previously, 3 PCBs (101, 153, 138) were detected in all sediment samples and 4 PCBs (156, 167, 189 and 195) were under limit of quantification. The total

concentrations of PCBs ($\sum_{28}\text{PCBs}$) ranged from 17.9 to 301.9 $\mu\text{g kg}^{-1}$ dw. The highest concentration was detected at STP1 (301.9 $\mu\text{g kg}^{-1}$ dw) on the corner of old basin where occurred loading/unloading of cargos (e.g. scraps), touristic vessels, urban discharges and ship maintenance activities. The lowest $\sum_{28}\text{PCBs}$ was determined for STP5 collected from fishery basin with concentration reaching 17.9 $\mu\text{g kg}^{-1}$ dw. Other sampling sites, $\sum_{28}\text{PCBs}$ were present at the level between 19.6 (STP14) and 91.4 $\mu\text{g kg}^{-1}$ dw (STP2).

These 28 PCBs included 7 PCBs congener's indicators ($\sum_7\text{PCBi}$ i.e. CB 28, 52, 101, 118, 138, 153 and 180), which are the most frequently detected in the environment and 12 high toxicity and persistent PCBs called PCBs dioxin-like ($\sum_{12}\text{PCB-DL}$ i.e. CB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189). $\sum_7\text{PCBi}$ detected in our sampling site ranged from 11.6 and 127.3 $\mu\text{g kg}^{-1}$ dw with mean value of 30.4 $\mu\text{g kg}^{-1}$ dw. PCB-DL with highly toxic and persistent in the environment (Kimbrough et al., 2010; Tanabe and Minh, 2010) which can cause toxic effect particularly in endocrine system (Schantz, 1996; Rice and Hayward, 1997) were also detected in our sediment samples. $\sum_{12}\text{PCB-DL}$ varied between 1.4 and 111.2 $\mu\text{g kg}^{-1}$ dw with mean value of 12.4 $\mu\text{g kg}^{-1}$ dw. The average concentration of $\sum_7\text{PCBi}$ represents 55.2% while the $\sum_{12}\text{PCB-DL}$ represents 22.6% of $\sum_{28}\text{PCB}$. The highest concentration of $\sum_7\text{PCBi}$ and $\sum_{12}\text{PCB-DL}$ were observed in STP1 with concentration reaching $\sum_7\text{PCBi} = 127.3 \mu\text{g kg}^{-1}$ dw and $\sum_{12}\text{PCB-DL} = 111.2 \mu\text{g kg}^{-1}$ dw respectively. These results show that PCBs contamination is detected in old basin of Tripoli harbour due to the presence of different sources of pollution.

The significant concentration of PAHs, and PCBs detected in STP1 may be related to water circulations which are mainly influenced by North East winds direction dominant in this area so we suggest that the pollutants are transported from different sources via waves then accumulated in the corner of the old basin but unfortunately no study was prepared in this field by Harbour Authority that can be referred on it.

Fig. 2 shows, the PCBs ($\sum_{28}\text{PCBs}$, $\sum_7\text{PCBi}$ and $\sum_{12}\text{PCB-DL}$), PAHs and Me-PAHs concentrations for all sediments samples in Tripoli harbour basins.

Most PAHs was detected and quantified in all samples except for station STP4. Dominance of high molecular weight PAHs with 4-rings (Pyr, Fluo, BaA, Chry) and 5-rings (BbF, BkF, BaP, DahA) were detected with 38.18% and 42.68% respectively (Fig. 3). The 2- and 3-rings PAHs represent only 0.92% and 12.50% respectively, due to their higher water solubility and their lower stability towards biodegradation process (Quantin et al., 2005). No significant variation was observed for the composition of Me-PAHs between 2-, 3- and 4-rings. The average compositions were 32.71%, 34.47% and 32.82% respectively for 2-, 3- and 4-rings Me-PAHs. It is interesting to note that lower molecular weight of PAHs (2- and 3-rings structures) are produced from petroleum products, fossil fuels and biomass incomplete combustion at low to moderate temperature and natural diagenesis, while high molecular weight of PAHs (4- or more rings structures) are produced at high temperature (Yuan et al., 2001; Mai et al., 2002). In our sediment samples, the predominance of high molecular weight compounds with 4-rings or more were detected in all samples (Fig. 3).

Each PCBs congener has different biological activity and toxicity due to the differences in the number and position of chlorine atoms in the molecular structure. In addition to toxic effect exert by PCB-DL mentioned previously; also, neurotoxic effects have been observed for the ortho-substituted congeners, with two or more ortho-chlorines (Rice and Hayward, 1997; Schantz, 1996). The composition of the PCBs congeners in sediment samples obtained from Tripoli Port was dominated by the content of 4 and 6Cl CB with 29.35% and 28.56% respectively (Fig. 3). Therefore the abundance of higher-chlorinated congeners indicates that

Table 2
Individual concentration of PCB, PAH and Me-PAH in $\mu\text{g kg}^{-1}$ dw for 15 sediment samples in Tripoli harbour, Lebanon.

Compounds	SPT1	SPT2	SPT3	SPT4	SPT5	SPT6	SPT7	SPT8	SPT9	SPT10	SPT11	SPT12	SPT13	SPT14	SPT15	Average
<i>PAHs</i>																
Nap	13.0	16.0	9.	11.6	9.0	10.3	5.3	10.8	11.2	17.7	10.2	6.3	5.2	4.6	6.7	9.8
Acy	15.5	5.5	5.3	6.0	2.4	3.7	2.2	2.8	3.5	3.0	2.7	0.7	0.9	0.9	2.4	3.8
Ace	18.6	6.0	9.0	8.8	5.1	12.0	3.2	4.4	5.3	7.5	5.4	1.9	2.1	1.4	3.7	6.3
Fl	21.3	7.5	7.7	6.9	5.9	12.3	3.1	7.7	5.1	8.6	4.8	3.6	3.1	15.3	7.9	8.1
Phe	159.5	85.7	101.4	110.2	87.7	215.8	44.9	75.1	66.5	87.4	83.1	29.6	34.7	50.4	58.3	86.0
Ant	53.4	45.3	25.7	34.2	33.4	42.1	15.6	13.1	11.4	15.7	24.9	9.9	9.9	70.9	19.7	28.3
Pyr	225.2	77.0	194.2	149.3	128.9	339.0	50.4	33.2	68.8	47.7	82.2	8.7	13.4	6.5	20.5	96.3
Flu	290.3	114.9	232.7	209.2	154.8	369.6	82.4	76.4	116.9	70.6	100.2	14.4	22.3	60.7	60.1	131.7
BaA	210.1	52.1	162.6	282.1	98.9	343.1	31.6	33.1	56.1	55.1	46.3	4.5	21.3	6.5	27.2	95.4
Chry	262.2	54.6	122.6	196.0	78.5	243.5	29.9	40.8	51.8	53.0	44.5	4.4	14.7	4.6	23.3	81.6
BF	637.2	158.1	355.6	420.7	254.3	625.6	71.3	66.7	160.3	79.9	105.8	30.6	20.9	11.6	42.5	202.7
BkF	112.8	25.78	58.20	75.99	46.71	88.70	19.3	7.22	24.2	8.93	19.01	9.02	4.21	3.39	6.66	34.0
BaP	458.3	184.1	210.0	309.3	172.5	436.7	74.4	53.5	98.6	93.4	132.5	66.0	48.0	126.4	63.1	168.5
DhA	112.3	72.1	65.9	64.1	48.5	88.5	40.8	24.3	37.4	34.1	41.5	30.2	18.3	–	35.7	47.6
BghiP	44.4	33.7	25.9	28.2	20.5	41.4	13.6	11.5	14.3	13.4	16.4	12.5	10.2	–	9.16	19.7
IDP	92.3	75.2	55.4	51.0	44.7	92.4	19.5	38.3	34.7	31.6	21.2	18.0	13.8	–	26.5	41.0
Σ 16 PAHs	2726.4	1013.6	1641.2	1963.6	1191.8	2964.7	507.5	498.9	766.1	627.6	740.7	250.3	243.0	363.2	413.4	
<i>Me-PAHs</i>																
1-MeN	23.2	46.0	22.1	275.1	18.5	12.0	6.1	38.0	47.2	81.2	17.4	8.7	11.4	4.2	14.8	41.7
2-MeN	26.0	33.6	12.8	139.1	8.3	5.3	3.1	19.9	31.2	44.5	9.5	5.2	5.7	2.3	7.0	23.6
1.2-DMN	32.7	45.0	30.5	383.8	28.5	15.4	9.6	51.1	102.7	104.7	28.4	17.9	16.4	7.6	25.5	60.0
1.6-DMN	15.6	21.3	10.8	109.0	8.19	6.06	3.24	19.1	40.6	39.43	10.3	6.0	5.8	2.9	7.8	20.4
2.6-DMN	18.0	27.0	16.3	47.5	5.0	2.8	4.8	7.0	65.3	15.8	12.5	8.5	7.8	4.1	13.3	17.0
1-MePhe	36.3	49.7	33.2	49.5	35.3	44.1	10.8	25.7	15.8	38.2	22.0	4.3	10.5	2.5	16.1	26.3
2-MePhe	49.4	59.0	42.3	65.7	41.5	44.3	9.3	36.1	18.0	46.0	32.8	5.1	11.8	3.2	18.1	32.2
3/9-MePhe	26.7	52.7	44.0	68.1	38.8	56.7	15.0	25.3	19.0	34.7	28.7	4.6	9.5	3.0	17.4	29.6
2-MeAnt	46.0	24.4	12.5	20.7	11.1	13.6	4.4	9.7	7.0	14.7	9.5	1.8	3.5	1.0	5.8	12.4
1.7-DMP	55.1	45.4	32.5	48.0	29.8	39.9	12.5	29.3	15.2	30.9	29.5	8.5	11.3	8.8	20.8	27.8
Retene	75.2	68.9	17.2	31.6	20.3	138.7	16.0	16.6	32.2	25.4	106.2	20.8	28.1	2.8	49.4	43.3
1-MeFluo	34.1	23.9	14.2	20.7	9.5	12.8	0.4	7.3	6.2	4.5	4.5	3.7	1.5	1.3	6.3	10.1
3-MeFluo	36.2	13.8	6.7	9.5	5.6	29.7	0.5	5.3	7.8	7.7	3.5	3.5	2.7	1.0	4.7	9.2
1-MePyr	37.4	54.4	61.4	96.8	46.7	48.7	1.4	33.7	26.2	33.2	28.2	5.9	9.3	2.6	24.5	34.0
4-MePyr	34.2	48.1	40.4	61.8	26.7	26.4	0.8	21.5	17.6	17.3	13.8	5.8	4.6	1.5	10.7	22.1
3-MeChry	115.1	80.1	85.2	140.0	62.1	71.9	3.2	50.3	87.3	82.5	48.4	12.6	15.3	2.8	26.2	58.9
6-MeChry	63.9	33.2	51.4	70.8	38.1	45.8	1.2	19.8	31.3	28.3	21.1	6.6	10.7	2.5	10.6	29.0
Σ 17 Me-PAHs	725.1	726.5	533.5	1637.7	434.0	614.2	102.3	415.7	570.6	649.0	426.3	129.5	165.9	54.1	279.0	
<i>PCBs</i>																
CB8	–	–	–	–	–	–	–	–	2.8	–	–	–	–	–	–	2.8
CB18	8.8	5.5	2.3	–	–	5.2	–	3.3	2.6	3.5	–	2.7	4.6	3.2	5.6	4.3
CB28	–	9.75	7.5	–	2.9	16.5	2.1	4.4	2.5	9.7	5.5	4.7	10.8	4.6	–	6.7
CB52	18.5	8.6	3.1	–	3.21	5.56	1.44	2.68	4.24	7.1	3.6	2.5	3.7	2.6	4.1	5.1
CB44	7.5	4.5	2.4	–	–	3.9	1.5	2.1	2.4	4.6	2.5	1.8	3.1	1.9	3.2	3.2
CB66	10.7	10.8	4.9	–	2.2	5.7	2.4	4.3	4.5	6.9	4.4	2.5	3.7	2.4	6	5.1
CB101	25.4	7.6	4.9	4.9	2.5	4.5	2.2	3.6	5.2	6.4	4.7	2.1	2.1	1.7	4	5.5
CB81	10.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	10.1
CB77	48.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	48.3
CB123	–	1.3	–	–	–	–	–	–	–	–	–	–	–	–	–	1.3
CB118	11.1	4.67	2.8	–	–	2.3	1.2	–	3.2	4	1.9	1.2	1.1	0.9	2.5	3.1
CB114	–	0.9	–	–	–	–	–	–	–	–	–	–	–	–	–	0.9
CB153	28.3	7.8	6.6	6.1	2.4	2.6	3.2	2.5	6.3	4.1	3.1	0.9	0.9	0.8	2.1	5.2
CB105	3.6	1.6	2.5	–	–	–	–	–	–	–	–	–	0.6	0.5	–	1.8
CB138	31.1	12.7	8.7	5.7	2.2	1.5	2	2	2.8	4.5	4.1	3	1.4	1	1.6	5.6
CB170	10.9	3	2	–	–	–	1.4	0.9	2.1	–	–	–	–	–	0.8	3.0
CB126	5	2.3	1.2	–	–	–	–	–	–	–	–	–	–	–	–	2.8
CB128	2.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	2.2
CB157	9.76	–	–	–	–	–	–	–	–	–	–	–	–	–	–	9.8
CB156	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CB169	23.3	6	6	9.7	2.4	1.7	2.8	1	5	2.4	–	–	0.4	–	0.8	5.1
CB180	12.9	4.4	2.4	–	–	–	0.6	–	2.1	–	–	–	–	–	–	4.5
CB 187	29.7	–	–	–	–	–	–	–	–	–	–	–	–	–	–	29.7
CB167	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CB189	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CB195	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CB206	3.94	–	–	–	–	–	–	–	–	–	–	–	–	–	–	3.9
CB209	0.85	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.9
Σ 28 PCBs	301.95	91.42	57.3	26.4	17.81	49.46	20.84	26.78	45.74	53.2	29.8	21.4	32.4	19.6	30.7	

“–”: not detected.

anthropogenic pollution has influenced the Port of Tripoli basins (Hong et al., 2005; Mai et al., 2005). Due to high solubility and volatility of lower chlorinated congeners, transport via surface runoff and atmospheric processes of these compounds can be occurred

easily. Also, during their transport in the atmosphere these congeners can be degraded by hydroxyl radicals (Mandalakis et al., 2003). Therefore, only small amount of lower chlorinated congeners deposit into marine sediments (Jönsson et al., 2003), which lead

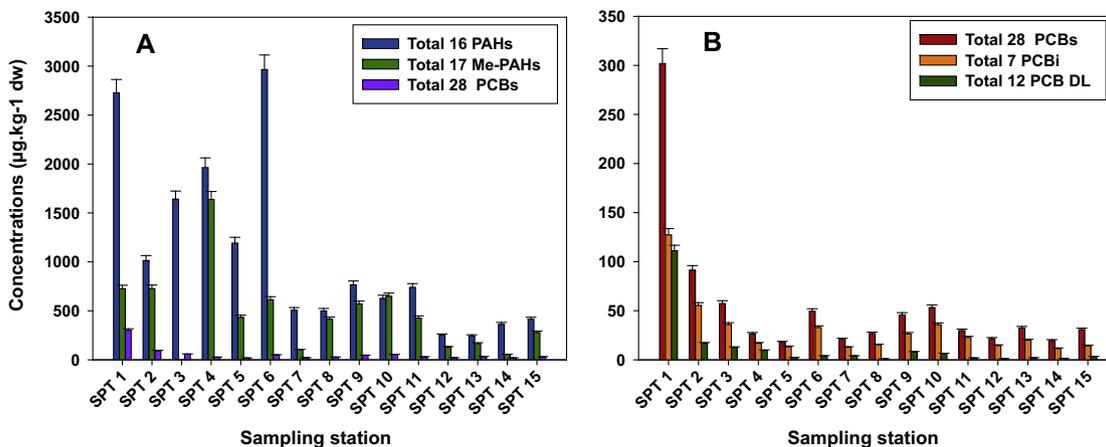


Fig. 2. Σ_{28} PCBs, Σ_7 PCBi and Σ_{12} PCB-DL concentration in Tripoli harbour basins.

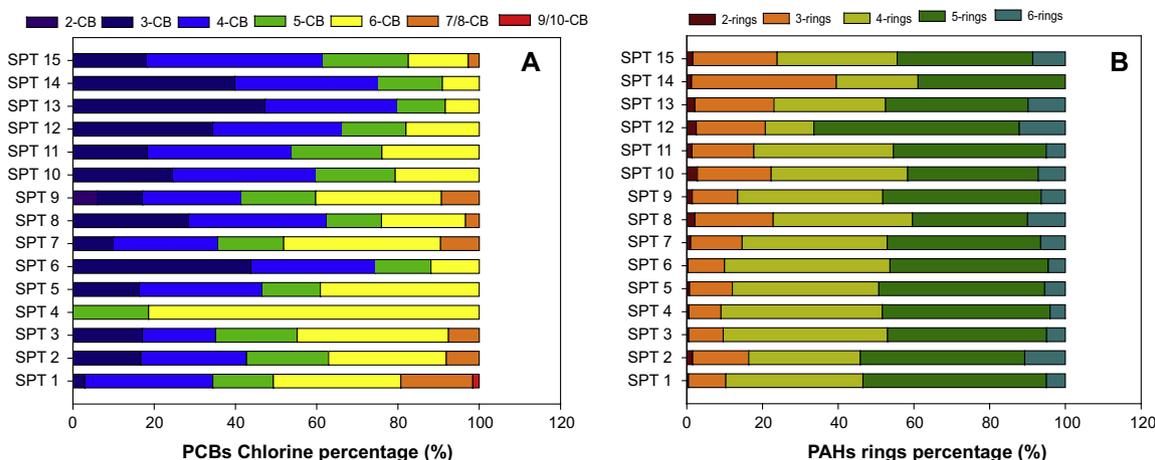


Fig. 3. PCBs and PAHs composition profile in the sediment samples collected from Tripoli harbour.

to higher level of high chlorinated PCBs congeners in the marine sediments. In our case the percentage of 5Cl and 6Cl CBs reached 16.8% and 28.6% respectively; and 3Cl and 4Cl reached 15.6% and 29.4% respectively (Fig. 3). These results suggest the presence of multiple sources of PCBs pollution in Port of Tripoli basins. The higher chlorinated PCBs can be due to the atmospheric deposition unintentionally released from port equipment, generators, ships, vehicles and trucks exhaust (Brož et al., 2000; Hong et al., 2005; Aries et al., 2006; Shibamoto et al., 2007; Liu et al., 2009). Also, the minor contribution of urban discharges, surface water runoff, harbour activities (e.g. ships maintenance) can be demonstrated by the presence of lower chlorinated PCBs in Port basins.

In general, anthropogenic PAHs are emitted as a mixture into environment (Tobiszewski and Namiesnik, 2012), which can be attributed to petrogenic and/or pyrogenic sources. Pyrogenic process responsible of PAHs inputs characterized by high abundance of high molecular weight PAHs and parent PAHs (non-alkylated PAHs). The petrogenic process is characterized by high abundance of low molecular weight and alkylated PAHs (Baumard et al., 1998). In this study, five molecular diagnostic ratios involve pairs of PAHs and Me-PAHs with the same molar mass and similar physicochemical properties ($Ant/(Ant + Phe)$, $Fla/(Fla + Py)$, $BaA/(BaA + Ch)$, $CO/(CO + C1)$ P/A and $CO/(CO + C1)$ F/P) are used for the identifying pollution emission sources contributing to PAHs released in Tripoli harbour basins (Yunker et al., 2002, 2012; Tobiszewski and Namiesnik, 2012).

For mass 178, $Ant/(Ant + Phe) < 0.10$ suggests pollution of petroleum origin, while a ratio > 0.10 indicates a dominance of combustion (Budzinski et al., 1997; Yunker et al., 2002). For mass 202, $Flu/(Flu + Pyr) < 0.40$ is consistent with petroleum inputs; a value between 0.40 and 0.50 indicates liquid fossil fuel (vehicle and crude oil) combustion and a ratio > 0.50 indicates grass, wood, or coal combustion (Budzinski et al., 1997; Yunker et al., 2002). For mass 228, $BaA/(BaA + Ch)$ suggested that ratio < 0.20 indicates petroleum inputs, a ratio between 0.20 and 0.35 indicates a mixed sources (either petroleum or combustion), and a ratio > 0.35 indicates combustion sources (Yunker et al., 2002, 2012). Also, for homologues alkyl PAHs ratios $CO/(CO + C1)$ P/A < 0.5 indicates petroleum or combustion sources and a ratio > 0.50 indicates coal or wood combustion or urban aerosols (Simo et al., 1997). For $CO/(CO + C1)$ F/P < 0.5 indicates petroleum sources and a ratio > 0.50 indicates combustion sources (Yunker et al., 2002, 2012).

The results showed that the combustion of biomass (wood and grasses) and coal is the predominance source of PAHs contamination of Tripoli Port sediments. Two example of cross plot of various ratios are showed in Fig. 4. The deposition of coal dust generated during the loading/unloading and storage of coal into Port of Tripoli are the major origin for Tripoli Port (Fig. 4). Moreover, the predominance of high molecular weight (HMW) confirms the origin of PAHs resulting from high combustion process such as engine emissions from port equipments, maritime transport, vehicles traffic (highway) and diesel trucks (Transit activities) (Mostert et al.,

2010; Tobiszewski and Namiesnik, 2012; Feng et al., 2012). Although, these results suggest the predominance of pyrogenic sources of PAHs contamination but we cannot ignore PAH derived from shipping activities, including ship discharges (ballast and/or bilge water) and oil spills in harbour basins. However, PAHs released by petrogenic sources are characterized by LMW which are preferentially biodegraded and dissolved compared to HMW derived from combustion and are preferentially adsorbed to particulate matter than deposits into sediments (Nemr and Abd-Allah, 2003). These characteristics lead to greater concentration of HMW in sediments than LMW and thus the predominance of PAHs derived from combustion sources.

Taking into account the correlation between PAHs isomers and PCBs concentrations as reported by Fernández et al. (2012) and Duan et al. (2013), and high chlorinated PCBs found in sediment samples in Tripoli harbour, we suggest that PCBs were mainly produced also by pyrogenic process due to the combustion of organic matter as reported in the literature (Pereira et al., 1980; Kjeller and Rappe, 1995; Rose and Rippey, 2002; Rose et al., 2004). There are no natural sources of PCB. PCBs detected in Tripoli harbour could be originated from unintentionally atmospheric deposition released from port equipment, generators, ships, vehicles and trucks exhaust. Furthermore, the contribution of sewage outfall, surface water runoff, harbour activities (e.g. ships maintenance) can be demonstrated by the presence of lower chlorinated PCBs in Port basins, which are easily dissolved in water (Mandalakis et al., 2003; Duan et al., 2013).

Indeed, POPs into atmosphere derived from combustion can enter the water surface directly by gaseous exchange across the air/water interface, dry deposition of airborne particulate matter, by rainfall, and transported by storm water runoff (Hoffman et al., 1984; Dickhut and Gustafson, 1995; Dickhut et al., 2000; Tsai et al., 2002; Oros et al., 2007) so we suggest that the direct and indirect inputs of POPs can affect the distribution of POPs in sediments samples of Tripoli harbour. In addition, due to their hydrophobic properties (low water solubility K_{ow} (PAHs) = 10^{-7} to 10^{-10} mol/m³) and strong affinity for organic matter (Culotta et al., 2006; Acquavita et al., 2014) POPs tend to accumulate in fine grained sediments. For our case, a geotechnical investigation Report was prepared for Tripoli harbour by (Hatem, 2002) shows that the sediments types within old basin are consisted an approximately 7 to 10 m thick layer of clayey sand to sandy clay with gravel and pebbles sometimes cemented (conglomeratic). For the new basin sediments are consisted of dark, greenish, grey, stiff to very stiff calcareous silty clay to clayey silt (marl) and traces of organic materials and peat were identified. Along principal break-

water, an approximately 5 m thick layer of calcareous silty sand to clayey sand with gravel and pebbles sometimes cemented (conglomeratic) underlying by an approximately 5 m thick layer of soft to medium stiff brown sandy to silty clay with gravel. The clay content in Tripoli harbour sediments is on the order of or greater than 30%. Therefore, we suggest also that the quite random distribution and concentration of POPs in Tripoli harbour sediments mainly can be due to the adsorption of POPs in the small particles (clay), which have a greater capacity of adsorption due to their greater specific surface area (Xia and Wang, 2008). Also, that the shipping and maritime activities which lead to water and sediment movement and the remobilization of these pollutants influenced this distribution.

In order to assess ecotoxicological risks, the concentration of total cancerogenic PAHs (\sum_6 PAHs CARC) are calculated. \sum_6 PAHs CARC for our sediment samples ranged from 126.5 at STP13 to 1675.0 $\mu\text{g kg}^{-1}$ dw at STP6. The highest concentrations was observed in STP1, STP4 and STP6 with concentrations reached 1623, 1203 and 1675 $\mu\text{g kg}^{-1}$ dw respectively, which indicate the influence of Tripoli basins by fishery activities (STP6), ship maintenance (STP4) and sewage outfall. Total PAHs (\sum_{12} PAHs) and total PCBs (\sum_{28} PCBs) concentrations were compared to sediment Quality Guidelines (SQGs) which provide an effective basis tool to evaluate the potential biological adverse effect on aquatic organism caused by contaminated sediments (Long et al., 1995). Two biological effects-based approaches including: the ERL/ERM (Effect range low/Effect range median) developed by Long and Morgan (1990) and the TEL/PEL (Threshold effect level/Probable effect level) developed by Macdonald et al. (1996) were applied to assess the ecological toxicity of total PAH and PCBs concentrations (\sum_{12} PAHs and \sum_{28} PCBs) in sediments collected from Port of Tripoli basins. According to SQGs, the classification of biological adverse effects are expected rarely (<ERL/TEL) with minimal-effects range (incidence of effects < 25%), occasionally (\geq ERL/TEL and <ERM/PEL) with possible-effects range, and frequently (\geq ERM/PEL) with a probable-effects range (incidence of effects > 75%) (Long et al., 1995; Cardellicchio et al., 2007).

For Tripoli Port sediment, the total PAHs concentration (\sum_{12} PAHs) was observed exceeded TEL values at 6 samples (40% of total samples) (Table 3) but still below PEL. Therefore the results showed that the biological adverse effects of PAHs that are expected occasionally for these samples collected from fishery basin and old basin of harbour closed to sewage outfall and ship maintenance areas. For others samples, the biological adverse effects that are expected rarely with \sum_{12} PAHs are not exceeded TEL values. The total of PAHs concentrations (\sum_{12} PAHs) for all

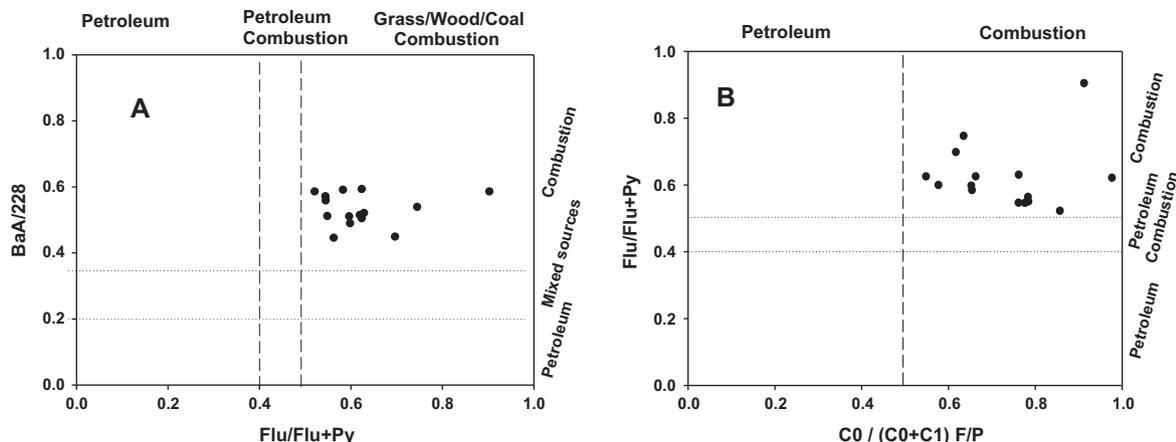


Fig. 4. (A) Cross plots of Flu/Flu + Pyr vs BaA/228. (B) $C_0/C_0 + C_1$ F/P vs the Fl/Flu + Pyr.

samples are below ERL were the biological adverse effects are rarely expected. Moreover, the classification of PAHs pollution levels which include low, moderate, high, and very high pollution levels when the concentrations of total PAHs are 0–100 ng/g, 100–1000 ng/g, 1000–5000 ng/g, and >5000 ng/g respectively (Baumard et al., 1998; Rahmanpoor et al., 2014). Based on this classification, sediments samples from Tripoli harbour basins varied between 243 and 2965 $\mu\text{g kg}^{-1}$ dw; so we suggest that it could be considered as moderate to high polluted with PAHs.

Total PCBs concentration ($\sum_{28}\text{PCBs}$) was exceeded TEL values at 11 samples (73% of total samples) (STP1, STP2, STP3, STP4, STP6, STP8, STP9, STP10, STP11, STP13 and STP15) (Table 3), but still below PEL except for STP1 was exceeded PEL value (Table 3). Therefore, the biological adverse effects of PCBs that are expected occasionally for the overall of Tripoli port basins. In 1990, Maritime Navigation and Ports Authority of France was established «Géode» classification (Groupe d'Etude et d'Observation sur le Dragage et l'Environnement) for dredged materials in ports sediments. Therefore, based on this classification all samples sediments in Tripoli harbour basins were below N1 level (500 $\mu\text{g kg}^{-1}$ dw) which we suggest that no environmental problems related to PCBs during dredged activities (Caplat, 2001).

The present paper is the first study on the evaluation of organic contamination level in Tripoli harbour. Our work provides a data base about two classes of persistent organic pollutants (PCBs, PAHs and Me-PAHs) in sediments collected from 15 stations of Tripoli harbour Basins. Multiple sources can be associated to PAHs and PCBs pollution into the harbour basin. However, the diagnostic ratios indicate that pyrogenic process is the dominance source. It is characterized by the abundance of high molecular weight of PAHs resulting from coal dust and the combustion of biomass and coal. However, the minor contribution of petroleum product produced by shipping activities, accidents oil spills and leakage from boats and ships, sewage outfall and fishery activities is due to the vulnerability of petroleum PAHs for degradation. Moreover, petroleum PAHs are characterized by low molecular weight PAHs that are more soluble in water. In order to determine the coefficient distribution between sediment and water, become necessary to quantify PAHs in water samples in Tripoli basins. The evaluation of ecotoxicological risk based on SQGs suggests that the biological adverse effects of PAHs are expected occasionally for fishery basin and old basin of harbour. In addition, the concentration of total PAHs in Tripoli basins varied between 243 and 2965 $\mu\text{g kg}^{-1}$ dw, could be considered as moderate to high polluted with PAHs

according to Baumard et al. (1998) classification. Concerning the PCBs contamination the biological adverse effects are expected occasionally for the overall of Tripoli Port basins. Based on these results, it is now urgent to adopt adequate pollution control strategies particularly in this harbour basins where the remobilization of these organic pollutants occurred frequently from sediments due to dredged activities and the continued development of Port activities which lead to intensive maritime transport into Tripoli harbour.

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Table 3

$\sum_{12}\text{PAHs}$ and $\sum_{28}\text{PCBs}$ obtained from 15 stations in Tripoli Port compared to TEL/PEL and ERL/ERM values.

Samples	$\sum_{12}\text{PAHs}$ ($\mu\text{g kg}^{-1}$ dw)	$\sum_{28}\text{PCBs}$ ($\mu\text{g kg}^{-1}$ dw)
STP1	1839.8	301.9
STP2	720.8	91.4
STP3	1146.1	57.3
STP4	1387.9	26.5
STP5	825.8	17.9
STP6	2116.7	49.5
STP7	383.8	20.9
STP8	375.3	26.8
STP9	532.8	45.8
STP10	493.8	53.2
STP11	578.4	29.8
STP12	180.3	21.6
STP13	194.0	32.4
STP14	348.3	19.6
STP15	328.7	30.7
TEL–PEL	655–6676	22–189
ERL–ERM	4022–44,792	23–180

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