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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 μg kg^{-1} dw, total Me-PAH concentrations ranged from 54 to 1638 μg kg^{-1} dw, while total PCB levels ranged from 18 to 302 μg 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.

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 northwestern 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 m^2, with a water area of 1,500,000 m^2, and a land area that consists of 950,000 m^2, and a 550,000 m^2 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 lixiviate) 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),

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