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Review

Overview of sediments pollution by PAHs and PCBs in Mediterranean Basin: Transport, Fate, Occurrence, and Distribution

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Table of contents

Abstract	2
Introduction	3
Definition of POPs	4
Origin of different family of POPs	6
Regional and global initiatives and conventions	11
Behavior, Transport and fate of POPs	14
Occurrence and distribution in Mediterranean basin	20
Conclusion and Recommendations	28
References	32

Abstract

We reviewed 194 studies concerning POPs in Mediterranean basin; 38 % were related to the origin and emission sources, as well as their physico-chemical properties and transport processes and 62 % were related to \sum_{10-26} PAHs and \sum_{7-41} PCBs distribution in Mediterranean basin. Only 57% of Mediterranean countries with coasts on the Mediterranean Sea, have a published research papers about POPs. As results of the survey study: Italy, France, Spain and Egypt were identified as the main polluted Mediterranean countries. The highest concentrations were reported at areas influenced by harbor and industrial activities as the case of Gulf of Taranto (Italy), Lazaret Bay (France) and Napels Bay (Italy). However, lack of data is available for some area. We can suggest that Mediterranean Sea is in critical situation and some measures whether on global and regional scale were recommended in order to protect it and save the natural resources for the future generations.

Keywords: POPs, Pollution, Mediterranean Sea and Hotspots.

I. Introduction

The increasing of anthropogenic pressures during last decades pose a significant threat and act as an evolutionary force for ecosystems due to its global coverage (Dachs and Méjanelle, 2010). Large number of chemical substances was detected in the environment; some of them have been reported as persistent organic pollutant (POPs) because they exhibit high toxicity, long-range transport potential followed by persistence and bioaccumulation potential (Vallack et al., 1998). These chemicals come from various applications ranging from agricultural pesticides, pharmaceuticals, detergents, flame retardants, insulating materials, di-electric fluids, combustion by-products and other applications (Vallack et al., 1998; Muir and Howard 2006; Schwarzenbach et al., 2003). Then, they can be transported far from their emission sources to reach different environmental media via various processes depending on their physico-chemical properties (Zhang et al., 2005; Dachs and Méjanelle, 2010). Therefore, a rising concern about their potential environmental effects began after the first public warnings in the early 1960s, and grew stronger in the 1970s (Zhang et al., 2005; El-Shahawi et al., 2010), when has been started a great attention on scientific field to dealing with these effects associated with the occurrence and fate of POPs. Fifty years after this initial awareness of their potential harmful effects, a huge scientific work was done on the field of their source identification, transport, fate, and impact on ecosystems and humans. Scientific progress has led to the regulation of a few of them by national and international organisms and had an important impact on international legislation. Even after several decades of banning and regulated some POPs, residues of these compounds have been found in environmental matrices and biota and elicit chronic toxic effects (Arslan-Alaton and Olmez-Hanci., 2013). These persistent chemicals continue to cycle through food chain transfer, atmospheric, and hydrospheric transport on national and global scale (Van Oostdam et al., 2005). However, this field is still in its infancy in terms of being able to evaluate the total contamination present in ecosystems and its real impact on aquatic organisms and humans. Recently some studies proposed an ecological risk assessment approach which provides an adequate framework for evaluating the propabilities that ecological adverse effects may occur or are occurring as a result of organism exposure to one or more environmental stressors (US-EPA, 1998). In the case of sediment contamination, the sediment quality guidelines (SQGs), are usually adopted (Chapman and Mann, 1999; Gómez-Gutiérrez et al., 2007).

II. Definition and classification of POPs

Organic substances, which are persistent having long-lives in environmental matrices, bioaccumulative and possess toxic characteristics likely to cause adverse effects on human health and environment so are called PBTs (Persistent, Bioaccumulative, Toxic substances) (Hansen, 1998; Vallack et al., 1998; Jones and De Voogt, 1999). Depending on their mobility in the environment, PBTs could be of local, regional or global concern (Vallack et al., 1998; Piaggi et al., 2007). POPs are a subclass of PBTs. Under the auspices of the United Nations Economic Commission for Europe (UN-ECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP), a protocol on POPs has been drawn up in which POPs as defined as a set of organic compounds that possess toxic characteristics, are persistent, are liable to bio-accumulate, prone to long-range atmospheric transport and deposition and can result in adverse environmental and humans effect at the locations near and far from their source (UN-ECE, 1998a). POPs are classified in families in many cases, one of these families contains tens or hundreds of different compounds (for example there are 209 polychlorinated biphenyls (PCBs) congeners differing from each other by level of chlorination and substitution position, polycyclic aromatic hydrocarbons (PAHs)) (Jones and De Voogt, 1999; Dachs and Méjanelle, 2010). To date, POPs refer to pesticides, PCBs and PAHs compounds. Table 1 present a list of priority substances in the CLRTAP POPs protocol and substances also specified in UNEP Governing Council Decision 19/13c for initial inclusion in the global POPs convention are shown in bold.

POPs can be classified into two categories: intentionally produced chemicals including organochlorine pesticides such as: DDT, aldrin, endrin, merix, dieldrin, heptachlor, toxaphene, and chlordane, and industrial chemicals such as: PCBs and hexachlorobenzene (HCB) and unintentionally produced by-product like dioxins, furans and PAHs (Fiedler, 2003; Zhang et al., 2005, 2009; El-Shahawi et al., 2010) (Fig. 2).

a) Intentionally POPs

This category includes several compounds which can be divided into two types: organochlorine pesticides and industrial chemicals including PCBs (Kelce et al., 1995; Harner et al., 2006).

Industrial chemicals

PCBs are a class of organic compounds formed with 1-10 chlorine atoms attached to the biphenyl molecule (Fig. 1 B). There are 209 PCB congeners. They were used in industrial applications as fire resistant transformers, heat exchanger fluids, dielectric fluids, plasticizers, adhesives, chemical stabilizers in paints, insulating materials, flame retardant, in aluminum, copper, iron and steel manufacturing processing, in natural and synthetic rubber products and so on (Korytáret al., 2002). In 1966, PCBs were discovered as environmental pollutants for the first time and they have been found throughout the world in water, sediments, bird tissue, and fish tissue (El-Shahawi et al., 2010; Arias et al., 2015). Although their production ended in the late 1970s, the majority of the cumulative world production of PCBs are still in the environment. Indeed, their resistant to degradation allows them to persist in the environment for a long time and become widespread via atmospheric and water transport mechanisms (Korytáret al., 2002; Villa et al., 2003). Moreover, PCBs are often found both in the effluent and in the sludge of municipal wastewater. Therefore, there are considered as an important class of special wastes. Due to its abundance in environmental samples International Council for the Exploration of the Sea (ICES) were selected seven individual congeners (PCBs 28, 52, 101, 118, 153, 138 and 180) (Duinker et al., 1988). Growing attention was focused to the so-called dioxin-like PCBs (DL-PCBs). PCBs substituted in 2- or 3- substitution was found able to exhibit dioxin toxicity while in the 3,3,4,4,5 or 5 position was not considered to be DL-PCBs (El-Shahawi et al., 2010).

b) Unintentionally POPs

Organic compounds were produced as unwanted by-products of combustion or chemical process that take places in the presence of chlorine compounds emitted from both stationary and mobile sources (Vallack et al., 1998). They are divided into three types namely dioxin, furan and PAHs (Fig. 2). As following briefly description of PAHs compounds:

Polycyclic aromatic hydrocarbons (PAHs)

Organic chemicals are also classified as potential POPs and POPs-like compounds by many agencies (Zhang et al., 2009; El-Shahawi et al., 2010). They are constituted of two or more fused benzene rings in linear, angular or cluster arrangements, containing only carbon and hydrogen. The central molecular structure is linked by stable carbon-carbon bonds. They are formed during pyrogenic process like fossil fuel combustion, forest and prairie fires, by-products of industrial processing and present in petroleum products. A certain amount of PAHs are released into the environment via anthropogenic processes (UNIDO, 2000). They have been detected in soil, air, and sediments as well as on various consumable products. The United States Environmental Protection Agency (U.S. EPA) listed 16 PAHs on a list of priority pollutants since they are considered either possible or probable human carcinogens (El-Shahawi et al., 2010). 16 PAHs U.S. EPA and their chemical structures are given in Fig. 1 A.

III. Origin of PCBs and PAHs

i. Historic Production and use

Early of 1881, PCBs were firstly produced by Germans then their intensive industrial usage in America began in 1929 (Zhang et al., 2005). PCBs were used as heat exchange fluids in electric transformers and capacitors, and as additives in paint, carbonless copy paper, sealants and plastics till their legal banish in 1970s (UNEP chemicals, 1999). Since 1970, PCBs production was banned but some electrical supply equipment containing PCBs is still in use in different regions poses a continuous serious threat to the environment (Shao, 2001). The banned and restricted POPs are mentioned in table 1. While PAHs are formed during carbonaceous material burning and petrogenic process (Zhang et al., 2009). Table 1 shows the production period and emissions estimates of some POPs.

ii. POPs emission sources and source identification

POPs sources can be divided between primary and secondary. Primary sources are those directly related to chemicals application (e.g. accidentally released PCBs from old

equipment). Contrariwise, secondary sources are due to its cycling in the environment through transport and transformation processes after they enter the environment (e.g. volatilization of PCBs from soil, sediment and water, thus soils and surface waters become secondary sources). Usually, secondary sources are diffuse sources, while primary sources are point sources (Dachs and Méjanelle, 2010). All regulatory efforts have been focused in controlling the primary sources of POPs whereas their occurrence, fate and exposure in the environment are mainly controlled by secondary sources (Lohmann et al., 2007). However, these regulations have some problem with primary emission sources which still uncontrolled to a certain value due to their diffusive character (e.g. polychlorinated dibenzo-p-dioxins (PCDD/Fs), PAHs and de novo formation of PCBs) (Dachs and Méjanelle, 2010). Atmospheric pathways were identified as the major mode of long-range transport and global dispersal for most POPs (Lohmann et al. 2007). In case of PCBs, there has been an extensive debate whether their atmospheric levels were mainly due to environmental cycling (e.g., Harrad et al., 1994; Jeremiason et al., 1994), or due to primary emissions (e.g., Jaward et al., 2004c; Robson and Harrad, 2004; Hung et al., 2005b). Recent studies attribute these to the continuing diffusive atmospheric emissions in densely populated areas (Jaward et al., 2004c) without confirmation whether these are due to primary or secondary sources (Hsu et al., 2003; Uraki et al., 2004). Whereas, higher molecular PAHs due to their strong sorption to atmospheric particles were controlled primarily by atmospheric emissions (Dachs and Eisenreich, 2000; Lohmann and Lammel, 2004), because PAHs act as “single hoppers” (Lohmann et al. 2007). Therefore, currently the main research topic is to identify the predominant sources due to its importance in terms of regulations and mitigation measures.

At the present time, there is a challenge for scientists to create an approach to identify POPs emission sources. Recently, PAH diagnostic ratios were used as a tool for identifying and assessing pollution emission sources enable to distinguish PAH pollution originated from petroleum products, petroleum combustion and biomass or coal burning. Most diagnostic ratios involve isomer pairs of parent and alkyl-substituted PAHs with the same molar mass and similar physico-chemical properties assumed that they undergo similar environmental fate processes (Tobiszewski and Namieśnik., 2012). These ratios allow identifying the origin of PAHs in different environmental media: air, water, sediment, soil, as well as aquatic species. Numerous studies show that diagnostic ratios change in value during phase transfers and environmental degradation. They are

sensitive to particle size and color and seasonal changes as a result of photo-degradation (Kavouras and Stephanou, 2002) (Dvorska et al., 2011). In Mediterranean aerosol, the most photo-reactive components, benz[a]anthracene (BaA) and benzo[a]pyrene (BaP), show depletion between urban and remote areas indicating that vehicle emissions as a primary source (Sicre et al., 1987; Gogou et al., 1996; Tolosa et al., 1996). The use of PAH diagnostic ratios has recently been criticized (Galarneau, 2008; Katsoyiannis et al., 2007; Zhang et al., 2005) because they are not usually conservative in the environment. Some PAHs ratios with mass 202 and 276 such as FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) are more conservative than ANT/(ANT + PHE) and BaA/(BaA + CHR) with mass 176 and 228 which are a photosensitive ratios (Tobiszewski and Namieśnik., 2012). Therefore, mass 276 and 202 isomers have the greatest range in stability and hence good indicators to distinguish between petroleum and combustion sources, whereas masses 278 and 228 show little promise as such indicators (Yunker et al., 2002). In general, PAHs lighter than Pyrene (PYR) and Fluoranthene (FLA) tend to accumulate in the gaseous phase, whereas PAHs heavier than BaP and CHR are mainly bound on particles. Therefore, some studies focus on the use of diagnostic ratios based on PAH concentrations in particulates only without taking into consideration the partitioning of PAHs between gas and particles in the atmosphere (Yunker et al., 2002; Tasdemir and Esen, 2007). In fact, their uses require an understanding of the relative thermodynamic stability, sources characteristics and composition changes of different PAHs between source and receptors. PAHs were found as a mixture in the environment and PAHs ratios are considered to be characteristic of a given emission source. Therefore, they recommended to apply them for strong, well characterized emission sources and for samples collected close to the source (Tobiszewski and Namieśnik, 2012). Misinterpretations due to wrong assumptions of diagnostic ratios can occur for particular sources to prevent it more than one diagnostic ratio should be used to at least four to seven ratio evaluations listed in Table 2 to confirm the results. Yunker et al. (2002) have reported that the C0/C0+C1 P/A and F/P ratios are more useful for source assignments than the alkyl homologue maxima, and the C0/C0+C1 ratio for F/P is a better indicator of combustion than P/A. However, the fact that contradictory results are obtained with different diagnostic ratios does not mean that the results are wrong but is related to their sensitivity to condition sites and these last should be take into consideration during data analysis. For PCBs, sources identification were based primary on the analysis of possible source emissions

at each sampling site or close to it, and gathered data for similar case from literature. Recently, the practical component analysis (PCA) is a new technique commonly used to evaluate these correlations between pollutants and their possible sources in order to identify the predominant one.

iii. Origin of POPs in Mediterranean Sea

Mediterranean basin is relatively a shallow and semi-enclosed basin divided into ten sub-basins (Fig. 3) with limited water exchanges are renewed through Gibraltar straits from water Atlantic Ocean every 89 to 90 years (Gabrielides, 1996; Zhang et al., 2009). Its volume is about 3.75 million km³ and its maximum and average depths are about 5120 m and 1538 m respectively (Gabrielides, 1996). The lack of tides and weak coastal currents induce the accumulation of pollutants rather than their removal or dispersion. The evaporation exceeds rainfall and river runoff (Berrojalbiz et al., 2011). Whereas, the construction of dams on the major rivers were reduced their seasonal high flows and consequently inhibit the cleaning phenomena of contaminant deposited on the continental shelf (Anna Gómez-Gutiérrez et al., 2007). In addition, it is considered as oligotrophic basin where oligotrophy dominant gradient increases from West to East in terms of primary productivity (Turley et al., 2000) and autotrophic biomass (Pitta et al., 2001). The main driving forces in the Mediterranean Sea are related to the urbanization, tourism, industrial production, intensive agriculture, ports and shipping activities (Gómez-Gutiérrez et al., 2007; Dachs et al., 2010; Berrojalbiz et al., 2011). Recently, Gómez-Gutiérrez (2007) has reviewed in its study assessment to Mediterranean Sea that the cities and river inputs pose an increasing pressure onto the Mediterranean coastal areas, which may cause a negative impact in coastal and marine ecosystem, and subsequent risk on natural resources (Anna Gómez-Gutiérrez et al., 2007; Berrojalbiz et al., 2011). Moreover, the Mediterranean basin is not subjected only to an important riverine runoff but also to an intensive atmospheric deposition of these contaminants (Castro-Jimenez et al., 2010). All these features besides its oceanographic characteristics has a significant implications for the accumulation of contaminants from point and diffuse land based sources for a long time and turn Mediterranean basin vulnerable to POPs (Gabrielides, 1996; UNEP/MAP, 2001; Zhang et al., 2009). Therefore, the Mediterranean sea has been recognized a special concern from the

environmental point of view specially after confirmed that act as a sink for these POPs (UNEP/MAP, 1999a,b). With evidence of long-range transport to regions where they have never been used or produced, their consequent adverse effects on environment and humans in the whole globe. The international community, has prompted actions at regional and global scale that address to reduce and eliminate the releases of POPs (Loganathan and Kannan, 1994; Jones and de Voogt, 1999) by a number of regulations leading to banned or restricted the global use and production of POPs in most developed countries by the late 1970s, but it continued until the 1980s in some of the Mediterranean countries, where they are still used until today (Anna Gómez-Gutiérrez et al., 2007 ; Berrojalbiz et al., 2011). And, by a series of international conventions which might contribute to more effective regulations and promote the marine pollution monitoring and management programs (Gabrielides, 1996; Vallack et al., 1998).

IV. Regional and global initiatives and conventions

a) POPs Global initiatives

There have been several milestones of international chemical management considering POPs such as the United Nations Economic Commission for Europe (UNECE) Convention on Long Range Transboundary Air Pollution (CLRTAP) and Stockholm Convention on POPs.

The CLRTAP POPs protocol: In 1997, within the framework of the UNECE Convention on Long Range Transport of Air Pollution (CLRTAP, 1979) the UNECE region (comprising eastern and western Europe, Canada and the United States) was established the final draft of UNECE CLRTAP Protocol. The protocol is structured in 20 articles and eight annexes. It represents a comprehensive set of provisions to control, reduce or eliminate production, total annual emissions, discharges, emissions and losses of POPs and develop and maintain emission inventories for the substances listed in its annexe. It is considered as an international initiative and instrument to control the risks from POPs. It identifies priority substances to be addressed. Among 107 substances presented in the initial list, 16 priority substances were identified for initial inclusion in this protocol comprising 11 pesticides, 2 industrial products and 3

unintentional by-products (Table 1). The need for emission inventories for POPs in the CLRTAP protocol oblige the involved parties to submit in annual summary report of their national emission data (UNECE, 2002), and made it available through the internet (e.g., Vestreng et al., 2006).

Stockholm Convention: It is considered as an important instrument for international action to protect humans and the environment against POPs. Briefly, this Convention was established under the auspices of the United Nations Environment Programme (UNEP). It was intended to reduce and/or eliminate the worldwide use then release of 12 original POPs substances or groups of substances which are called the “dirty dozen” or “legacy” POPs shown (in bold) in Table 1 (UNEP, 2001). It was agreed by 90 countries and opened for signature in May 2001 in Stockholm but came into force in May 2004 (Vallack et al., 1998; Zhang et al., 2005; El-Shahawi et al., 2010). The Annex D of Article 3 includes a strong incentive for early prevention action to avoid the introduction of new POPs into the market (Arslan-Alaton and Olmez-Hanci., 2013). Ongoing effort was done to further develop relevant control strategies under the UNEP Stockholm Convention (UNEP, 1999/2001; Fiedler, 2007). This agreement requires from signatories to control the production, import, export, use, release and disposal of all these 12 POPs. And, obliged them to develop a national implementation plans to draw up POPs emission inventories. E.g. so-called toolkit has been developed to assist countries in quantifying dioxin emissions in a consistent manner (UNEP, 2005) and the new NORMAN EMPODAT: ECOTOX Database which will be used as an important data source of emerging pollutants to support European commission (EC) (Slobodnik, 2015). Because that UNEP was conducted a regionally based assessment of sources, environmental levels, transport pathways and effects of the 12 POPs, the Mediterranean region was the first where these plans and policies were implemented (UNEP, 2002, 2003).

b) POPs Regional initiatives

In fact, the POPs chosen for the initial inclusion in CLRTAP convention focus on the atmospheric pathway as a transport route for POPs. Whereas the aquatic ecosystem is also one of the main routes by which POPs can reach remote regions which impetus Mediterranean states to meet in Barcelona in 1975 to the elaboration convention for the protection of the Mediterranean Sea against pollution namely “Barcelona Convention”. This convention is in order to improve the environmental management and sustainable

development of the region and protect their common sea (Gabrielides., 1996; Vallack et al., 1998).

Barcelona Convention: In 1976, Mediterranean states adopted the convention for the protection of the Mediterranean sea against pollution (Barcelona Convention) and two of its related protocols: (i) the protocol for the prevention of pollution of the Mediterranean sea by dumping from ships and aircraft (Dumping protocol) and (ii) the protocol concerning cooperation in combating pollution of the Mediterranean sea by oil and other Harmful substances in cases of emergency (Gabrielides., 1996). Twenty Mediterranean countries have been ratified this convention and these two related protocols. Then in 1980, 1982 and 1994 two other protocols have been adopted by these Mediterranean states are respectively: (i) the protocol for the protection of the Mediterranean against pollution from Land-Based Sources (LBS protocol); (ii) the protocol concerning Specially Protected Areas (SPA protocol) and (iii) Protocol was adopted in Madrid for the Protection of the Mediterranean sea against pollution resulting from exploration and exploitation of the continental shelf and the sea-bed and its subsoil. In addition to all these protocols this convention includes also an action plan namely Mediterranean Action Plan (MAP), and the Mediterranean Marine Pollution Monitoring and Research Program (MED POL) as a scientific and technical component.

Mediterranean Action Plan (MAP): This action plan is an excellent example of cooperation forum between Mediterranean states is not limited to monitoring of marine pollution but includes also aspects relevant to environment and development. It consists of some main components aiming to protect the Mediterranean sea and its resources from pollution: (i) Integrated planning of the development and management of Mediterranean resources from the socio-economic point of view, coordinated programme for research, monitoring and exchange of information; and for assessment the state of pollution and protection measures (MED POL Program). Moreover, it is intended to assist the Mediterranean governments in formulating their national policies and to improve their ability to identify various development patterns and to make choices regarding the appropriate allocation of resources.

MED POL PROGRAMME: MED POL program is the scientific and technical component of MAP and it was the first one to be initiated in 1975. The aim of MED POL is to assist the technical capabilities of Mediterranean institutions from less developed and provide a data base about marine pollution by gathering of information about sources,

environmental levels and effects of pollutants in the Mediterranean region. Involves more than 100 Mediterranean research and monitoring institutions and it is coordinated unit center is located in Athens (Gabrielides, 1996).

However, despite all these international interventions started since 1972s, there is still a significant gap in reliable data due to the lack of information for many pollutants and geographical areas in particular that located in the southern and eastern parts of the Mediterranean Sea with the exception of the Egyptian coast. The northwestern basin is the most studied area followed by the Adriatic sub-basin. This large spread between the northern basin and the southern and eastern basins of the Mediterranean Sea reflect the socio-economic patterns of the countries surrounding this basin where is a clear relationship between national Gross Domestic Product (GDPs) and the application of environmental control and management measures (Gómez-Gutiérrez et al., 2007). Therefore, an urgent need to investigate and survey new regions in this neglected part of the Mediterranean basin. The purpose of this overview is to provide comprehensive understanding information about POPs with focus on PCBs and PAHs; properties, occurrence, sources, distribution, transport, and fate and produce a picture of the amount of PCBs and PAHs concentrations in sediments of the whole of Mediterranean Sea.

V. Behavior, transport and fate of POPs

The physicochemical properties which were attributed to POPs dictate their behavior, transport and fate in the environment (Jones and De Voogt, 1999; El-Shahawi et al., 2010). These depend on the structure of the molecule and the nature of the environment. They are hydrophobic, lipophilic and semi-volatile substances enable to move via rivers, marine waters and atmosphere long distance before their adsorption onto soil and sediments and subsequently their bioaccumulation in biota up to food chain (Guzella et al., 2005; Grassi et al., 2010). They possess some characteristics such as toxic, persistent, bio-accumulative and prone to long-range transport (El-Shahawi et al., 2010). Therefore, according to their specific partitioning property and their major modes of transport behavior, Wania (2003) have classified as flyers, multi-, single hoppers and swimmers. For example PCBs, can be classified as multi-hoppers (Wania, 2003, 2006) while PAHs act as single hoppers (Lohman et al., 2007). Due this multi-hop nature of POPs to relate their deposition rates to emission rates is a very complicated matter.

However, the two main processes determining their persistence into atmosphere are the degradation and deposition or recycling rates, which are controlled by temperature and reaction with the OH-radical. The half-life values were estimated at two days, two months and six months in air, water and soil/sediment respectively (Vallack et al., 1998). If six months is estimated as a half-life, it will be necessary to observe a decrease of their concentrations for at least two half-lives or 1 year, but actually they vary in time and space (Vallack et al., 1998). POPs were introduced to the coastal environment by a number of processes then they are subject to biogeochemical cycling, sinks, and bio-accumulation processes. Figure 4 shows schematics of the processes driving the environmental fate of POPs in coastal waters. Due to these processes POPs are transported horizontally and vertically, accumulated in bottom sediments, move from the atmosphere to the ocean and back. The atmospheric deposition across air-sea interface exchange is the main input route for POPs to the marine environment and its ecosystems. Different processes contributing to this exchanges of POPs are vapor-particle partitioning, wet deposition, dry deposition with particles and diffusive air-water vapor exchange. Within the atmosphere and surface water additional processes affecting this exchange are aerosol-vapor partitioning, and partitioning and sedimentation in the water column (Wania et al., 1998).

Vapor-particle partitioning: in the atmosphere is mainly controlled by their absorption in organic carbon which is the most abundant component in atmospheric fine aerosols. This has a strong influence on the fate of POPs in the aquatic and terrestrial environment (Pankow, 1994a, b; Heintzenberg, 1989). The octanol-air partition coefficient (K_{OA}) give an excellent characterization of partitioning from air to aerosols (Vallack et al., 1998). For example, concentrations of atmospheric Σ_{41} PCBs are ranged from 389 to 1410 $\text{pg}\cdot\text{m}^{-3}$ in the gas phase and from 71 to 78 $\text{pg}\cdot\text{m}^{-3}$ in the aerosol phase in off-shore Barcelona (García-Flor et al., 2009) and In Banyuls-sur-Mer, France, Σ PCBs were found as 30.7- 858 $\text{pg}\cdot\text{m}^{-3}$ in the gas phase and 12.8 - 41.2 $\text{pg}\cdot\text{m}^{-3}$ in the aerosol phase.

Wet deposition: The precipitation scavenged POPs from the atmosphere both as vapors dissolved in the raindrops and bound to particles which are incorporated in the rain. This process is directly related to the intensity and the spatial and seasonal variations of precipitation (Wania et al., 1998).

Dry deposition: Dry deposition velocities (V_D) depend on particle and surface properties, such as particle size and density, humidity, meteorology and most of all wind speed. Highest settling velocities are displayed by the coarse-particles which settle by both gravitation and turbulence impact (Fig. 4). A positive correlation was established between wind direction, wind speed, and atmospheric PCB concentrations, which are supported by the high dissolved concentrations of PCBs in the coastal and marine surface waters, and especially by the concentrations found in the surface microlayer and sediments (Arslan-Alaton and Olmez-Hanci., 2013). A water surface is peculiar with respect to dry particle deposition in that surface roughness changes with increasing wind speed from smooth to rough, and particles may grow due to water vapor condensation at the high relative humidity near the ocean surface, thereby increasing their deposition velocities (Jenkin, 1984). The Dry deposition flux of coarse particles bound to POPs have been found dominant closer to land-based sources (Broman et al., 1990; Holsen et al., 1991, 1993; Pirrone et al., 1995). The measured and estimated V_D for POPs which tend to fall are in the range 0.0013-0.011 $\text{m}\cdot\text{s}^{-1}$, with a geometric mean of 0.0046 $\text{m}\cdot\text{s}^{-1}$. Some studies has derived a V_D of 0.0037 $\text{m}\cdot\text{s}^{-1}$ for particle-bound PAHs (McVeety and Hites, 1988) while for total PCB are 0.0038-0.0051 $\text{m}\cdot\text{s}^{-1}$ (Holsen et al., 1991). Indeed, the information on size distributions for POPs is still extremely limited making it difficult to even estimate applicable mass median diameters.

Diffusive air-water vapor exchange: POPs can diffuse across the air-water interface; both in the vapor phase in air and the dissolved molecules in water participate in this diffusive transport which is driven by a deviation from chemical equilibrium (escaping tendency or fugacity) between the air and water phase (Wania et al., 1998). This process is reversible and counteracts any fugacity gradient which may arise from precipitation scavenging, dry particle deposition, air mass changes over a water body, and temperature gradients. The net vapor transfer accounts approximately 50-85% of the atmospheric deposition of OCs to the sea (GESAMP, 1989). And, approximately a fourth to a third of the atmospheric input is due to vapor absorption for the rather water soluble, and thus easily scavenged (e.g HCHs) (Wania et al., 1998). Molecular diffusivities in both air and water increase with temperature. This means that the rate of evaporation (N_{WA}) increases with temperatures for air side, whereas the rate of absorption (N_{AW}) decreases with temperatures for water side. POPs have limited water solubilities (S_W), leading in a good ability to associate to various forms of particulate and mainly to dissolve organic carbon which comprises more than 90 % of total organic

carbon (TOC) in water. This interaction is due to the dissolution of POPs into a porous organic matrix, rather than surface adsorption process (Schwarzenbach et al., 1993). The particulate and dissolved organic carbon partition coefficient (K_{OC} and K_{DOC}) is an equilibrium expression commonly employed when comparing the equilibrium partitioning of POPs in different aquatic particulate and dissolved matrices. Log K_{DOC} of most POPs are in the range 4-8 (Wania et al., 1998). The vertical advection of water masses, gravitational settling of particulate matter, and mixing of water masses by eddy and turbulent diffusion processes contribute to the removal of POPs from surface layers (Wania et al., 1998). Within water column the partitioning of POPs onto particulate and colloidal organic matter or efficient removal of POPs from the mixed surface water layer reduces the fugacity of the compounds in the water-column and consequently reduces volatilization rates.

Vertical transport of POPs within the water-column: Settling velocity (V_p) within water column depends on the size and density of the particles and on types of water flow around the settling particle either is laminar or turbulent. Theoretical value of V_p increases about four orders of magnitude over the particle size range 1-100 μm (Officer, 1981). During their settling the differences in V_p between different sizes particles enable large particles to scavenge small particles. In addition, collisions of small colloids and particles causing small particles to aggregate, grow and settle (Wania et al., 1998; Strukov, B. 2006). This process can also occurs upwards (resuspension of particles) induced by currents or wave action which become important in coastal areas as well as shallow open sea such as Mediterranean Sea (Fig. 4). Other processes such as bubbles created during the breaking of waves, the raindrop splashing especially during heavy rainstorms associated with strong winds and the extensive photosynthesis of marine algae can contribute to the transfer of POPs from the water to the atmosphere (Wania et al., 1998). Hence, it has become clear this close relationship between the water column's biological pump and the atmospheric long-range transport potential of POPs (Dachs et al., 2002; Scheringer et al., 2004; Strukov, B. 2006).

Effect of Temperature and seasonal variation

The deposition pathways of POPs depend on the temperature and seasonal variation and subsequently in the global and regional distribution behavior and fate of POPs in the environment (Mackay and Wania, 1995). In the case of vapor- particle partitioning, POP concentrations on particles are higher at low temperatures within the temperature range

encountered in global environment, i.e. within -40 to +40°C. This tendency was present in both the vapor phase and sorbed phases has been namely “semi-volatility” (Wania et al., 1998). Whereas for dry deposition the effect of temperature is no significant, the decrease in diffusivity at lower temperature may result in lower deposition velocities V_D of very small particles while seasonal differences have a stronger impact on the V_D . Moreover, V_D is dependent on surface roughness and a snow/ice surface tends to be smoother than a water surface so the snow may be a very efficient scavenger of POP vapors (Czuczwa et al., 1988; Wania et al., 1998). For wet deposition, vapor scavenging should become more efficient with decreasing temperature, but unfortunately very limited field measurements are available to confirm this temperature dependence. Particle scavenging is dependent on meteorological and physical factors, such as the vertical distribution of particles and precipitation intensity. The equilibrium partitioning between air and water, as expressed in Henry's Law constants (H), is temperature dependent (Wania et al., 1998).

Based on these deposition and re-cycling routes different partitioning coefficients were predicted such as: K_{OA} , aerosols-vapour partition coefficient (K_p), octanol-water partition coefficient (K_{OW}), air-water partitioning (K_{AW}), K_{OC} and K_{DOC} (Wania et al., 1998; Vallack et al., 1998). However, the relative importance of these processes is also mainly dependent on POPs specific properties. Due to their hydrophobicity POPs are characterized by high values of the K_{OW} and thus have high affinity to organic matter to which they sorbed (Jurado et al. 2004) (Fig. 5). Water solubility (S_w), vapor pressure and biodegradability are low and decrease with an increasing degree of PAHs rings and chlorine substitution while hydrophobicity and sorption tendency increase (Arslan-Alaton and Olmez-Hanci., 2013). The Variation of the S_w , Log K_{OW} and Log K_{OC} for PAHs and PCBs according to the numbers of (A) PAHs rings and (B) PCBs Chlorine atoms is show in Fig. 5. POPs with same physicochemical properties have similar trends, pathways and fate in the environment.

Grain size and organic matter content

They play an important role in the sorption behavior of POPs on atmosphere and water column. Due to their low S_w and high K_{OW} and K_{OC} (Fig.5), POPs have high affinity for solid matrices (Ozcan et al., 2009; Zhao et al., 2010). Thus, PAHs were mainly associated with the fine aerosol fraction which is dominant during winter season (e.g. Van Vaeck and Van Cauwenberghe, 1978; Aceves and Grimalt, 1993; Gardner et al.,

1995). Differences were also found between PAHs molecular weight and degradability (Pistikopoulos et al., 1990; Venkataraman and Friedlander, 1994; Allen et al., 1996). And, between urban and rural sites were related to aerosol ageing processes (e.g. Allen et al., 1996). Particle size distribution for PCBs over a limited particle size spectrum (1 - 40 μm) showed quite uniform concentrations across this size range with slightly higher concentrations for the smaller aerosols (Holsen et al., 1991). Has been reported for Milwaukee Harbor sediment that 75 % reduction of PAHs within the fraction < 63 μm comprising the clays and silt while for coal-derived material no significant reduction of PAH concentrations during the biotreatment process (Accardi-Dey and Gschwend, 2002). This mean that PAHs and POPs in general were associated with the lighter density fraction creating primarily strongly bound with coal-derived particles as well for PCBs bound to airborne soot particles present in light size fraction < 63 μm in the atmosphere before depositing in the sediment (Ghosh et al., 2003). PAHs and PCBs in the sediment tend preferentially to accumulate in these carbonaceous particles where they may be strongly bound making them less available for biological uptake and release into the overlying water (Wania et al., 1998; Ghosh et al., 2003). Such migration of PCBs and PAHs into a more strongly sorbing matrix has significant implications for assessment of sediment quality criteria. The cycling of POPs in the environment is depended also to their absorption by organic carbon.

POPs have resistance to photolytic, biological and chemical degradation and thus subjected to long-range transported (Vallack et al., 1998). This phenomenon is referred to bioavailabilities were the need to develop new technologies to reduce their emissions from some station sources and for sediment and soil treatment in some hotspot areas (Chu et al., 2006). PAHs partitioned with semi-solid, coal tar pitch are largely bioavailable than PAHs sorbed on coal or coke particles (e.g. Harbor Point sediment) and Log K_{OC} values for phenanthrene sorption on coal is about 6.3 - 6.4 and 5 for phenanthrene partitioning in coal tars (95 % carbon content) (Galiulin et al., 2002; Chu et al., 2006). However, PAHs may remain preferentially associated with original source materials such as coal tar pitch and may be available to microorganisms for biodegradation (Ghosh et al., 2003). An important process influence POPs level in soils and sediments which decrease due to the "ageing" effects producing non-extractable residues over time. Then it will remove the proportion of the POP available for environmental re-cycling and potentially that transferred into food chains (Hatzinger and Alexander, 1995). Fig. 6 is a conceptual graph illustrating the idea of changing

proportions of degradable, bioavailable and non-extractable fractions of POPs over time in soil and sediment.

As a consequence of this persistence, low SW and high Log K_{OW} , POPs can accumulate high levels in organisms. In aquatic ecosystem the primary routes of POPs is through active uptake of POPs bound particulate matter by filter-feeders and plankton (Fig. 5). A significant correlation between PCBs concentrations (C_P) and the biomass in Mediterranean Sea (PCBs; $R^2 = 0.58$, $p < 0.01$) was observed by Berrojalbiz et al., (2011). This has been hypothesized to be driven by the biomass dilution effect in plankton and biomass in Mediterranean Sea (Larsson et al., 2000). POPs such as PCBs, DDT and HCB bioconcentrate in phytoplankton (Berrojalbiz et al. 2009), bacteria (Wallberg & Andersson 2000), and bioaccumulate in higher trophic webs (Restrepo et al. 2005; Arias et al., 2015). Their resistance to chemical and metabolic degradation led to increase their concentrations in fatty tissue, this phenomenon namely biomagnification can lead to concentrations in top predators many orders of magnitude higher than in the environment (Gobas et al. 1999; Dachs and Méjanelle, 2010).

VI. Occurrence and distribution in Mediterranean basin

Mediterranean Sea is considered as a sensitive basin and a very interesting region for studies. Gabrielides (1996) has reported, based on some results selected during MED POL program, that the Mediterranean Sea (MS) in general still in very good health. While significant pollutant concentrations were found in the northwestern part of the MS in the vicinity of coastal areas in particular these close to industries and population centers. Sediments can be an important sink or sources for POPs to the atmosphere. Air-sea exchange is an interesting topic because it allows to the recognition of major continental inputs as well as an evaluation of their magnitude and area of influence (Garcia-Flor et al. 2009; Dachs and Méjanelle, 2010). Therefore, in order to draw a clear picture of the level of POPs pollution in the MS data regarding PAHs and PCBs concentrations in sediments were gathered from 192 studied sites during last thirty years until now of more than 121 authors published papers. Among twenty-one Mediterranean countries with coasts on the MS, only twelve countries have published research papers on POPs. The most studied sites are concentrated in the northwestern basin of MS and a significant gaps exist in the south and southeastern basins with the exception of the Egyptian coast and recently Lebanese coast, similar result were found also by Anna

Gómez-Gutiérrez et al., (2007). For PAHs, 33% of articles were reported for Italy, France (24 %), Spain (15 %), Egypt (11 %), Lebanon (5 %), Greece (4 %), Tunisia (3 %), Turkey and Morocco (2 %), Croatia and Slovenia (1%) and for PCBs; France (33 %), Spain (17 %), Italy (15%), Lebanon (8 %), Egypt (6 %), Greece (5 %), Portugal (4 %), Algeria (4 %), Turkey and Tunisia (3 %), Albany, Croatia, and Morocco (1 %).

Total concentrations of \sum_{10-26} PAHs and \sum_{7-41} PCBs in sediment samples collected from different studied sites in Mediterranean countries and references are presented in Annex 1 and 2. Fig. 7 shows the total mean concentrations of the \sum_{10-26} PAHs and \sum_{7-41} PCBs in the sediments for each Mediterranean country. Based on these concentrations, Mediterranean countries can be classified in the following order Italy > Egypt > France > Spain > Turkey > Croatia > Tunisia > Lebanon > Greece > Slovenia > Morocco for PAHs pollution (Fig. 7A) and in the order; France > Italy > Egypt > Spain > Lebanon > Croatia > Greece > Algeria > Turkey > Portugal > Morocco > Tunisia > Albany for PCBs pollution (Fig. 7B).

In fact, it is very difficult to separate harbors from industrial coastal areas, bays and lagoons due to the complexity and variability of anthropogenic contribution in these sites which receive industrial effluents, urban sewages, agricultural runoff, and riverine inputs and harbor activities. However, based on the characteristics of each site the data collected were divided into four categories; harbors and industrial coastal areas, Lagoons, Rivers and Estuaries and open Sea. In order to assess the influence of urban, rivers and harbors pressures separately and samples lying in the open sea are also considered. Fig. 8 show the contribution of these four categories in these total mean concentrations of the \sum_{10-26} PAHs and \sum_{7-41} PCBs in the sediments for each Mediterranean country.

PAHs and PCBs distribution in Mediterranean Basin

Harbors and industrial coastal areas were the most contaminated by the \sum PAHs in almost all studied in Mediterranean countries (Fig. 8a). Table 3 summarized the highest total concentrations of \sum PAHs in sediments collected from Mediterranean sites. In Italy, the highest PAHs concentrations were reported for Gulf of Taranto (262446 $\mu\text{g.kg}^{-1}$ d.w.) followed by Lazaret bay, France (48090 $\mu\text{g.kg}^{-1}$ d.w.) (Cardellicchio et al., 2007; Benlahcen et al., 1997) (Table 3). Gulf of Taranto was the most polluted site in Mediterranean Sea. This Gulf was influenced by multiple anthropogenic pressures

including harbors activities and industrial effluents of two industrial plants (i) the “ILVA” iron and steel factory, which is the most important steel production plant in Europe, and (ii) the “ENI” petroleum refinery where occurred a very intensive shipping activities, loading/unloading of petroleum products (Annicchiarico et al., 2011). In these two sites is clear that the combination of driving forces make the distinguishing between industrial and harbors pressures a very complex task. However, the influence of harbors pressures is demonstrated also by the concentrations found in Alexandria harbor in Egypt (13150 $\mu\text{g.kg}^{-1}$ d.w.), Naples harbor in Italy (31774 $\mu\text{g.kg}^{-1}$ d.w.), Ajaccio harbour in Corse-France (20440 $\mu\text{g.kg}^{-1}$ d.w.), Lazaret navy harbour in France (13010 $\mu\text{g.kg}^{-1}$ d.w.), Sfax-Kerkennah Coast in Tunisia (10720 $\mu\text{g.kg}^{-1}$ d.w.) and Barcelona harbor in Spain (10320 $\mu\text{g.kg}^{-1}$ d.w.) (Table 3). In Turkey, Tolun et al. (2001) have reported that ΣPAHs were 2500 - 25000 $\mu\text{g.kg}^{-1}$ d.w., while Telli-Karakoç et al., (2002) have found at 30000 - 167000 $\mu\text{g.kg}^{-1}$ d.w. The difference may be due to the location of sampling sites. In Croatia, the highest concentration in Rijeka Bay were found in the vicinity of a repair shipyard (12532 $\mu\text{g.kg}^{-1}$ d.w.). Above all, we can suggest that harbor sediments of MS were significantly polluted by the ΣPAHs .

Also, a significant PAHs contamination was found for lagoons in some Mediterranean countries. Highest ΣPAHs concentrations were found in Pialassa Baiona lagoon, in Italy in the range of 1000-135000 $\mu\text{g.kg}^{-1}$ d.w., (Vassura et al., 2005; Guerra., 2011). High concentrations were also detected in other Italian hotspot lagoons such as Venice Lagoon (65 - 48000 $\mu\text{g.kg}^{-1}$ d.w.) and Mar Piccolo in Taranto (380 - 12750 $\mu\text{g.kg}^{-1}$ d.w.) (Table 3). This significant organic pollutant enrichment in Venice Lagoon was observed near the industrial plants of Porto Marghera. While in Mar Piccolo, although urbanization influence (presence of nine sewages outfalls, aquaculture commercial fishing and small river inputs), highest level was found near to the harbor area of the Italian Military Navy due to the influence of shipyard activities. Obviously, harbors have the significant pressures in coastal areas leading to the accumulation of these pollutants; is a very complex systems, the pollution can be due to activities directly related to the port as the case of shipyard activities in Italian Military Navy harbor or not strictly related to harbor activities as the case of Venice lagoon where the pollution is due to the industrial units present inside the harbor. However, the scarce hydrodynamism and low water exchange seem lead to the decreasing the level of ΣPAHs with time in the range of 315 - 810 ; 15 - 389 and 20 - 502 $\mu\text{g.kg}^{-1}$ d.w. such as reported by Frignani et al., (2003), Secco et al., (2005) and Parolini et al., (2010) respectively (Table 3). Similarly to that suggested for

Pialassa Baiona lagoon this decrease of Σ PAHs may be due to special laws to preserve and improve its environmental quality and/or environmental re-cycling processes. In France, the highest Σ PAHs was observed at Thau and Berre lagoons at 59 - 7679 and 38 - 2323 $\mu\text{g.kg}^{-1}$ d.w. respectively. The concentration of Σ PAHs decreased in Berre lagoons to reach maximum concentration of 853 $\mu\text{g.kg}^{-1}$ d.w (Kanzari et al., 2003) (Table 3). However, the highest Σ PAHs increase in Bizerte lagoon in Tunisia from 447.1 $\mu\text{g.kg}^{-1}$ d.w. in 2005 to 2500 $\mu\text{g.kg}^{-1}$ d.w. in 2008 have been reported (Trabelsi and Driss, 2005; Louiz et al., 2008). This may be due to the increase of industrial units as well as population nearby.

The riverine inputs play an important role in the transition of PAHs to the MS in some countries. In France, highest Σ PAHs in the Rhone Delta (river mouth) were in the range of 1070 - 6330 $\mu\text{g.kg}^{-1}$ d.w., have been reported by Bouloubassi and Saliot (1993) while Lipiatou and Saliot (1991) have been found at 325 - 3182 $\mu\text{g.kg}^{-1}$ d.w. (Table 3). High Σ PAHs were also found in Griond estuary with the range of 185 - 4888 $\mu\text{g.kg}^{-1}$ d.w. An important contribution of PAHs to MS could be via rivers in Spain particularly for Llobregat River, Francolí River and Besós river with Σ PAHs reaching 3650, 3050 and 1299 $\mu\text{g.kg}^{-1}$ d.w., respectively (Eljarrat et al., 2001) followed by Po river in Italy (1800 $\mu\text{g.kg}^{-1}$ d.w), Nile river in Egypt (933 $\mu\text{g.kg}^{-1}$ d.w) and Abou Ali estuary in Lebanon (667.8 $\mu\text{g.kg}^{-1}$ d.w) (Table 3). Highest Σ PAHs reaching 210 000 and 610 000 $\mu\text{g.kg}^{-1}$ d.w, were found in two main river outfalls Dil Deresi and Doğu Kanalı in Izmit Bay in Turkey, respectively (Telli-Karakoç et al., 2002). Dil Deresi river receives the wastes from many factories and domestic sewage while Doğu Kanalı river carry the domestic sewerage of 36 large factories and wastes including wheels, stainless steel wire and glass, lamps, plastic, fermentation products, gas (Oxygen, nitrogen, argon), meat, medicines, food, electrolytic copper (Telli-Karakoç et al., 2002). Above all, we can consider that Izmit Bay is the most important hotspot in the Mediterranean Sea even more than Gulf of Taranto, Italy but is considered as an exceptional case by the author because that is not included in the comparison graphs.

The majority of samples were originated from coastal areas, as those are more accessible to monitoring. In Open Sea, the Σ PAHs concentrations of samples collected from Adriatic Sea, Aegean Sea and Northwestern Mediterranean Sea were 19 - 426 $\mu\text{g.kg}^{-1}$ d.w, 148 $\mu\text{g.kg}^{-1}$ d.w. and 119 $\mu\text{g.kg}^{-1}$ d.w., respectively (Table 3). While concentrations found in open sea of Soller, Majorca island, Spain located between the

Northwestern and Southwestern Mediterranean Sea were 8.4 – 18 $\mu\text{g.kg}^{-1}$ d.w. (Baumard et al., 1998b) and can be considered as background Levels. However, new studies are needed for the determination of Background levels of PAHs in each sub-basins of Mediterranean Sea.

Harbors and industrial coastal areas were the most contaminated by ΣPCBs in almost all studied concerning Mediterranean basins (Fig. 8b). Table 4 summarized the concentrations of ΣPCBs in sediments collected from some Mediterranean basins. The highest levels of PCBs in the Northwestern Mediterranean Sea were found in Cortiou near Marseille (France) with maximum concentration about 22900 $\mu\text{g.kg}^{-1}$ d.w. (Lecouffe, 1986) (Table 4). The main input of these pollutants in this area were the sewage outfalls from the urban area of Marseille (Gómez-Gutiérrez et al., 2007). Another important contribution of PCBs in the Tyrrhenian Sea derives from Naples Bay, one of the most highly industrialized and densely populated areas in southern Italy with maximum concentration of 3200 $\mu\text{g.kg}^{-1}$ d.w. (Baldi et al., 1983) (Table 4). In Ionian Sea, PCBs at Gulf of Taranto (Italy) is related to industrial sources and harbor activities with concentrations ranged from 85 to 1780 $\mu\text{g.kg}^{-1}$ d.w. (Annicchiarico et al., 2011). In the Southeastern part of the Mediterranean basin, high PCBs concentrations were observed in sediments of Port-Said and Alexandria harbor in Egypt (South Levantine Sea) with concentrations vary between 53 - 1500 $\mu\text{g.kg}^{-1}$ d.w and 0.9 - 1211 $\mu\text{g.kg}^{-1}$ d.w., respectively (Table 4). Recently, a study has been conducted in the east of North Levantine Sea. The concentration of PCBs has been detected at high level which reached 1303 $\mu\text{g.kg}^{-1}$ d.w. at Port of Beirut followed by Port of Jiyeh power plant (Table 4). In the south of the Northwestern Mediterranean Sea, the highest level found corresponds to the samples collected in the vicinities of the urban sewage outfall and a primarily treated wastewater disposal site at Barcelona coast (654 $\mu\text{g.kg}^{-1}$ d.w.) (Fernandez, 1991) (Table 4). In Adriatic Sea, PCBs pollution derives from Rijeka Bay in Croatia with maximum reaching 597 $\mu\text{g.kg}^{-1}$ d.w. (Table 4). In Aegean Sea, Okay et al. (2009) investigated that the total PCB levels in sediments along the industrialized coasts of Istanbul strait and a Marmara Sea island in Turkey were ranged from 0.179 to 539.746 $\mu\text{g.kg}^{-1}$ d.w. lower than Keratsini harbour, Saronikos Gulf in Greece which showed also elevated levels about 4.78 - 351.8 $\mu\text{g.kg}^{-1}$ d.w. (Galanopoulou et al., 2005). In the Southwestern sub-basin, high concentrations (323 $\mu\text{g.kg}^{-1}$ d.w) were found for Algerian coastal area close to the cities of Oran and Alger (Cousteau, 1979).

Coastal Lagoons show high levels of PCBs pollution at three Mediterranean countries (Fig. 8b). These highest concentrations were reported in Italy inside the lagoon of Mar Piccolo in Taranto (2 - 1684 $\mu\text{g.kg}^{-1}$ d.w.) and inside Venice lagoons (6 - 1590 $\mu\text{g.kg}^{-1}$ d.w.) (Cardellicchio et al., 2007; Frignani et al., 2001) mainly originates from the industrial and harbors activities as well as mentioned previously for PAHs pollution and particularly the discharge of domestic sewage from the city of Venice into this lagoon (Pavoni et al., 1998). In France, high levels of PCBs was detected at Berre lagoon at 468.8 - 541.4 $\mu\text{g.kg}^{-1}$ d.w. (Kanzari et al., 2012). Manzala Lake in Egypt showed also high contamination by PCBs (Yamashita et al., 2000) (Table 3).

The contribution of river inputs of PCBs in MS were observed at four Mediterranean countries; Spain, Italy, Lebanon and France (Fig. 8b). In Spain, the highest ΣPCBs reach 1772 $\mu\text{g.kg}^{-1}$ d.w. in the mouth of Ebro River (Fernández et al., 1999). While, other study conducted by Eljarrat et al. (2001) for Catalan coast where the samples were collected from ten rivers (Besós River, Ebre River, Falconera River, Fluvià River, Foix River, Francolí River, Llobregat River, Muga River, Ter River and Tordera River), the PCBs concentrations vary from 1.1 to 311 $\mu\text{g.kg}^{-1}$ d.w. Another contribution was observed from Tiber River in Italy with maximum concentration of 770 $\mu\text{g.kg}^{-1}$ d.w. (Puccetti and Leoni, 1980) probably reflecting the state of contamination when these products were still in production and usage in the region. In France, Arc River release the highest PCBs concentrations reaching about 467 $\mu\text{g.kg}^{-1}$ d.w. (Kanzari et al., 2012) followed by Rhone River at Fos Gulf about 416 $\mu\text{g.kg}^{-1}$ d.w. (Tolosa et al., 1995). Recent study in Lebanon shows that Abou Ali River has also high contribution of PCBs pollution in MS where the concentration was found at 339.4 $\mu\text{g.kg}^{-1}$ d.w.

The PCBs concentrations found in the open sea, far away from the coastal sources could be a reliable estimation of background levels of contaminants in Mediterranean sediments. The ΣPCBs found in the open sea in Northwestern Mediterranean Sea, Provençal basin (2 - 3 $\mu\text{g.kg}^{-1}$ d.w.), and Catalan basin, Spain (4 - 11 $\mu\text{g.kg}^{-1}$ d.w.), and North Adriatic Sea, Italy (3.2 - 58 $\mu\text{g.kg}^{-1}$ d.w.), Tyrrhenian Sea (0.88 - 1.3 $\mu\text{g.kg}^{-1}$ d.w.), Southwestern Sea, Algeria margin (9 $\mu\text{g.kg}^{-1}$ d.w.) and Ionian Sea, Albany (5 $\mu\text{g.kg}^{-1}$ d.w.) (Tolosa et al., 1995, Geyer et al., 1984; Burns and Villeneuve, 1983, 1985; Elder and Villeneuve, 1977b; Koci, 1998) (Table 4). By calculating the mean of minimum and maximum of these values, the interval background level of total PCBs is from 3 to 15 $\mu\text{g.kg}^{-1}$ d.w. Whereas, other background intervals ranging from 1 to 5 $\mu\text{g.kg}^{-1}$ d.w. and

from 1.2 to 2.9 $\mu\text{g.kg}^{-1}$ d.w. for 7 ICES PCBs was reported by Anna Gómez-Gutiérrez et al., (2007) and Tolosa et al. (1995), respectively. However, this interval is critical due the fact that we did not have more information about the number of PCBs congeners.

Obviously, the number of hot spots identified depends on the availability of data in each country, which does not imply that others may not exist but is not studied. Therefore we have an urgent need to study new sites in order to cover the whole Mediterranean basin and identify if any other hotspots area is present. The impact of large cities is demonstrated by the high concentrations of these pollutants found in their costal sediments (e.g. Taranto, Marseille, Naples, Geneva, Barcelona, Alexandria, Greece, and Alger and Oran) (Table 3 and 4). And in coastal lagoons of some countries (e.g. Pialassa Baiona, Mar Piccolo Taranto and Venice Lagoon in Italy, Thau and Berre lagoons in France, Bizerte lagoon in Tunisia, ŠKocjan in Slovenia and Manzala Lake in Egypt). Other hot spot areas identified in this study are Izmit Bay in Turkey, Lazaret Bay in France, Rijeka Bay in Croatia, Port Said in Egypt and Port of Beirut in Lebanon. And, high concentrations found in sediments at the mouth of the main Mediterranean rivers (e.g. Rhone, Llobregat, Francolí, Besós, Ebro, Po, Nile, Tiber, Arc and Abou Ali rivers) highlight the necessity of also considering these zones as contamination hot spots for the target contaminants.

The point sources of pollution, such as industrial units, river and sewage disposal outfalls, as well as diffuse sources like agricultural, industrial and urban runoff could give rise to the accumulation of POPs in the areas of influence of the presumed sources particularly in harbors basins and lagoons. These lasts are vulnerable to the accumulation of these pollutants due to low tidal currents and reduce water exchange which lead to localize the pollution in these areas and this was obviously observed in our study. Therefore, a particular concern should be taken for harbors where the coastal sediments are frequently remobilized (shipping, dredging) causing POPs desorption from sorbing matrix and dissolved phase to enter again the environmental cycle (Asher et al. 2007; Yan et al. 2008; Garcia-Flor et al. 2009). The maximum was found in harbor areas, which also exhibited the higher variability. To have a clearer picture, some studies conducted in some Mediterranean harbors were selected to identify the hotspots harbors in Mediterranean basin. Fig. 9 shows the concentration of ΣPAHs (I) and ΣPCBs (II) in sediment harbors of some Mediterranean countries.

As shown in Fig. 9 for Σ PAHs pollution, the hotspots harbors were found in the following order Naples harbor, Italy > Genoa Punta Vagno harbor, Italy > Ajaccio harbor, France > Genoa Polcevera harbor, Italy > Alexandria Eastern harbour, Egypt > Port of Bagnoli, Italy > Lazaret nay harbor, France > Barcelona Harbor in Spain while the high levels of PCBs pollution were found in Port-Said, Egypt > Port of Beirut, Lebanon > Alexandria harbor, Egypt > Naples harbor > Port of Jiyeh, Lebanon > Kerastini harbor, Greece > Tripoli harbor, Lebanon > Port of Bagnoli, Italy. Majority of harbors with high PAHs pollution were found in NWE except Alexandria harbor while the majority harbors with high PCBs pollution were found in the NLE and SLE. This can be explained that in the eastern and southeastern part of MS, some countries still used the equipment used in vessels and/or paints or other product containing PCBs and particularly in harbors. However, it is interesting to note that the Northwestern, the Adriatic and the Tyrrhenian sub-basins, South Levantine Sea and Aegean Sea are those exhibiting the highest levels of PAHs and PCBs and is consistent with the industrialization and population densities of some riparian countries whether located in east (Turkey, Egypt) or west (Italy, France and Spain). Whereas the mismanagement of environmental conditions in some developed countries also contribute to high level of pollution varied from moderate to high and can cause an adverse effect on aquatic organisms and can become a hotspots in the future.

During this study we faced some limitations that samples cannot be representative in some areas such as Izmit Bay in Turkey and the information about lithology of the continental shelf and sedimentation rate which can influence the accumulation process of POPs in surface sediments. However, the influence of these factors can be reduced by comparing samples from similar geographical areas. Sediment sampling (the depth of sampled layer) and number of PAHs and PCBs congeners were not determined for all studies can be a source of data dispersion. Moreover, the lack of more recent data does not allow drawing a definitive conclusion on the recent state of contamination by POPs in some areas. And, operational variability was another factor to address complicated data comparison for the same sites which decrease with years. Authors suggest that decline in concentrations at some studies site may be due to three reasons; improvement of environmental control measures, environmental re-cycling processes of these pollutants and the improvement in the analytical methodologies used during sampling and measurements.

VII. Conclusion and Recommendations

Human has greatly modified the biosphere by the release a great amount of POPs into the environments. Multiples anthropogenic activities contribute to this pollution directly and indirectly whether by primary or secondary sources. Their physicochemical characteristics as a toxic, persistent, bioaccumulative dictate their behavior, transport and fate in the environment. And because that prone a long range transport in the environment the POPs can reach areas as far as from their emission sources and accumulate in abiotic and biotic environmental matrices (e.g. air, water, sediment, soil and biota). In the environment these POPs are transported by multiple pathways including dry and wet atmospheric deposition and air-water surface exchange and they are subjected to fractioning and partitioning process between different environmental media. The influence of the size of particles and ambient temperature for both dry and wet deposition rate and air-sea exchange processes were also considered. Higher POPs concentrations were found close to urban source areas due to the importance of coarse particles and ambient temperature influence the equilibrium, mechanisms and kinetics of air-sea exchange of POPs. In marine ecosystem, the sediment is not considered only as final reservoir but both a sink and source of these POPs. Due to different environmental or anthropogenic events these pollutants can be remobilized and desorb to join the recycling environmental processes and accumulate in phytoplankton and aquatic organisms up to food chain. After that their impacts on environment and human health are well known major effort were done to more understand their environmental behavior and quantify their concentration in different matrices and final sinks. But our understanding of several key processes is largely incomplete due to imperfect parameterizations, lack of knowledge of potential processes (e.g. emissions and deposition rates), effect of surface and ambient temperature, uncertainties about partitioning coefficients, and incomplete global, regional and seasonal coverage of POP concentrations. Furthermore, the environmental cycling of these compounds has not been totally understood and huge uncertainties exist on their environmental distribution and fate on a global scale. Many international and regional initiatives were establishes such as Stockholm and Barcelona conventions to eliminate, regulate and control these POPs in the environment. But some challenges were faced in their effective implementation due to the presence of some exemptions for substances that there are no available alternatives (e.g. DDT), the difficulties for the elimination the use of these

substances and the existing stocks in an environmentally manner in some countries, to ensure that actual usage is limited to those authorized activities only and the need an alternative for these substances. Moreover, that CLRTAP protocol and UNEP Stockholm convention both of them focus on the atmospheric pathway as a transport route for POPs whereas the aquatic ecosystem is also one of the main routes by which POPs can reach remote regions. Although, the activities determined in MAP which considered as an effective cooperation network instrument and those doing during MED POL program which is intended to assist the Mediterranean governments in formulating their national policies and to improve their ability to identify various development patterns and to make choices regarding the appropriate allocation of resources and improve the technical capabilities of the institutions of less developed countries we still observed by several authors Gómez-Gutiérrez et al., (2007) and in this work a significant gaps in reliable data due to the lack of information for many pollutants and geographical areas in particular that located in the southern and eastern parts of the Mediterranean Sea with the exception of the Egyptian coast. Therefore, in order to contribute to fill some gaps a survey study of the distribution of some POPs concentrations (PAHs and PCBs) were conducted in this review on Mediterranean region make easier to conduct a similar study on global scale on the future. As results we observed numerous hotspots Mediterranean countries and several sub-hotspots areas in each one of them. Italy, France, Spain, Egypt and Turkey are the main Mediterranean countries contributed to PAHs and PCBs pollution of Mediterranean Sea. As far as the cities and their offshore areas leading to higher sediment contamination, by the target compounds in their surroundings due to their higher degrees of industrialization and urbanization are mostly concentrated in NWE, TYR, ADR, AEG and SLE (Egyptian coast) Sea. Relatively high contamination levels were detected in sediment samples collected from three stations including the bayous and harbors, lagoons and river mouths. The decline in concentrations observed in some areas can be explained by multiple ways, may be can due to the ecological politics of government and local authorities, environmental re-cycling processes and/or development in analytical methods used now by comparison to that used twenty to thirty years ago. In other hand, we observed an increase in some areas of other countries and intercountry. Although, the technical and analytical development we have also a great Lack in information also related to open sea and deep sediment to take a definitive conclusion but we can suggest that Mediterranean is in critical situation and is not in

very good health as reported by Gabrielides et al., (1996) nineteen years ago so the question is what will be the situation after ten or twenty years?.

Finally we recommend some measure should be taken in order to control and manage the release of these POPs into environment in order to protect it and save the natural resources for the future generations whether on global and regional scale as following:

On Global scale

- 1- Conduct more measurements of physicochemical properties of POPs including Henry's Law constants and partitioning coefficients as a function of surface and particle size, ambient temperature and salinity.
- 2- Conduct more study to monitor of legacy POPs, in water, air and biota in order to detect their trends and improve our understanding of their sources, occurrence, fate and ecological risk.
- 3- Implement a research program with the objective to assess the environmental risk of real complex mixtures of pollutants.
- 4- Develop a normalization procedures could account the differences in sediment characteristics (organic carbon content and particle size) as well as the implementation of quality assurance/quality control procedures are considered essential.
- 5- Develop new accurate methods to identify the predominant sources of POPs whether their environmental occurrence and impacts are dominated by primary and secondary sources which are important in terms of regulatory efforts whereas the present regulation consider in most cases the primary emissions of POPs.
- 6- Harmonized water and atmosphere legislations to promote the efficient control of organic and inorganic pollutants levels in many ecosystems.

On regional scale

- 7- Enhance collaboration and exchange information, experiences and best practices between all Mediterranean countries by creating a large co-operation between institutions, and social actors to coordinate the implementing of Barcelona provisions including MAP and MED POL Program which should continue to play a key role in capacity building and developing quality criteria standards throughout the region for the benefit of all.

- 8- Establish a new monitoring programs of POPs in different environmental matrix in many countries to fill the geographical data gaps, and promote the establishment an accredited institutional to ensure the sustainability of monitoring activities inside these countries in order to generate a comparable and accurate data.
- 9- Assist the technical capacities of less developed countries by involved them in workshops and projects in order to enhance their participation in regional policies and strategies and improve their knowledge about these POPs for the best management.
- 10- Establishment of an integrated strategic framework for POPs management including control policies essential to develop and use technologies for POPs control and remediation.
- 11- Adoption an integrated environmental assessment (IEA) approach that allows a broader participation of research community, industries and public in environmental assessment and decision-making there maybe scope for further voluntary activity by industries to support some research activities related to POPs.

c) References

- Accardi-Dey, A., Gschwend, P. M., 2002. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environmental Science and Technology* 36, 21 - 29.
- Aceves, M., Grimalt, J.O., 1993. Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. *Environmental Science and Technology* 27, 2896 - 2908.
- Alebic-Juretic, A., 2011. Polycyclic aromatic hydrocarbons in marine sediments from the Rijeka Bay area, Northern Adriatic, Croatia, 1998–2006. *Marine pollution bulletin* 62, 863 - 869.
- Allen, J.O., Dookeran, N.M., Smith, K.A., Sarofim, A.F., Taghizadeh, K., Lafleur, A.L. 1996. Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts. *Environmental Science and Technology* 30, 1023 - 1031.
- Annicchiarico, C., Buonocore, M., Cardellicchio, N., Di Leo, A., Giandomenico, S., Spada, L. 2011. PCBs, PAHs and metal contamination and quality index in marine sediments of the Taranto Gulf. *Chemistry and Ecology* 27, 21 - 32.
- Arslan-Alaton, I., Olmez-Hanci, T., 2013. Chapter 12: Sources of Environmental Pollution: Persistent Organic Pollutants. Istanbul Technical University, Faculty of Civil Engineering, Department of Environmental Engineering, 34469 Maslak, Istanbul, Turkey.

- Asher, B.J., Wong C.S., and Rodenburg L.A., 2007. Chiral source apportionment of polychlorinated biphenyls to the Hudson River estuary atmosphere and food web. *Environmental Science and Technology* 41, 6163 - 6169.
- Badawy, M.I., Emababy, M.A., 2010. Distribution of polycyclic aromatic hydrocarbons in drinking water in Egypt. *Desalination* 251, 34 - 40
- Bailey, R.E., 2001. Global hexachlorobenzene emissions. *Chemosphere* 43, 167 - 182.
- Bajt, O., 2008. The impact of road traffic on hydrocarbon content in the sediments of the Škocjan wetland. *Ann. Ser. Hist. Nat.* 18, 41 - 46.
- Baldi, F., Bargagli, R., Focardi, S., Fossi, C., 1983. Mercury and chlorinated hydrocarbons in sediments from the bay of Naples and adjacent marine areas. *Marine Pollution Bulletin* 14, 108-111.
- Barakat, A.O., Kim, M., Qian, Y., Wade, T.L., 2002. Organochlorine pesticides and PCB residues in sediments of Alexandria Harbor, Egypt. *Marine Pollution Bulletin* 44, 1421 - 1434.
- Barakat, A.O., Mostafa, A., Wade, T.L., Sweet, S.T., El Sayed, N.B., 2011. Distribution and characteristics of PAHs in sediments from the Mediterranean coastal environment of Egypt. *Marine Pollution Bulletin* 62, 1969 - 1978.
- Baumard, P., Budzinski, H., Garrigues, P., 1998a. Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean sea. *Environmental Toxicology and Chemistry* 17, 765 - 776.
- Baumard, P., Budzinski, H., Guarrigues, P., Dizer, H., Hansen, P.D., 1999. Polycyclic aromatic hydrocarbons in recent sediments and mussels (*Mytilus edulis*) from the Western Baltic sea: occurrence, bioavailability and seasonal variations. *Marine Environmental Research* 47, 17-47.
- Baumard, P., Budzinski, H., Michon, Q., Garrigues, P., Burgeot, T., Bellocq, J., 1998b. Origin and bioavailability of PAHs in the Mediterranean sea from mussel and sediment records. *Estuarine Coastal and Shelf Science* 47, 77 - 90.
- Benlahcen, K.T., Chaoui, A., Budzinski, H., Bellocq, J., Garrigues, P., 1997. Distribution and sources of polycyclic aromatic hydrocarbons in some mediterranean coastal sediments. *Marine Pollution Bulletin* 34, 298 - 316.
- Berrojalbiz, N., Dachs, J., Del Vento, S., Ojeda, M. J., Valle, M. C., Castro-Jiménez, J., Hanke, G., 2011. Persistent organic pollutants in Mediterranean seawater and processes affecting their accumulation in plankton. *Environmental science and technology* 45, 4315 - 4322.
- Berrojalbiz, N., Lacorte S., Calbet A., Saiz E., Barata C., and Dachs J., 2009. Accumulation and cycling of polycyclic aromatic hydrocarbons in zooplankton. *Environmental Science and Technology* 43, 2295-2301.
- Bihari, N., Fafandel, M., Hamer, B., Kralj-Bilen, B., 2006. PAHs content, toxicity and genotoxicity of coastal marine sediments from the Rovinj area, Northern Adriatic, Croatia. *Science of Total Environment* 366, 602 - 611.
- Bouloubassi, I., Roussiez, V., Azzoug, M., Lorre, A., 2012. Sources, dispersal pathways and mass budget of sedimentary polycyclic aromatic hydrocarbons (PAH) in the NW Mediterranean margin, Gulf of Lions. *Marine Chemistry* 142-144, 18 - 28.
- Bouloubassi, I., Saliot, A., 1993. Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH. LAB. PAH). *Oceanologica Acta* 16, 145 -161.
- Brevik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2007. Towards a global historical emission inventory for selected PCB congeners e a mass balance approach. 3. An update. *The Science of the Total Environment* 377, 296 -307.

Broman, D., NaÈf, C., Wik, M., Renberg, I., 1990. The importance of spheroidal carbonaceous particles (SCPs) for the distribution of particulate aromatic hydrocarbons (PAHs) in an estuarine-like urban coastal area. *Chemosphere* 21, 69 - 77.

Budzinski, H., Jones, I., Bellocq, J., Pie´rard, C., Garrigues, P., 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry* 58, 85 - 97.

Burns, K. A. and Villeneuve, J. P., 1983. Biogeochemical processes affecting the distribution and vertical transport of hydrocarbon residues in the coastal Mediterranean. *Geochimica Cosmochimica Acta* 47, 995 - 1006.

Burns, K.A., Villeneuve, J.P., Fowler, S.W., 1985. Fluxes and residence times of hydrocarbons in the coastal Mediterranean: how important are the biota? *Estuarine Coastal Shelf Science* 20, 313 -- 330.

Cardellicchio, N., Annicchiarico, C., Leone, G., Ragone, P., Rochira, M., 1989. Determinazione di idrocarburi policiclici aromatici in sediment del Golfo di Taranto. *Nuova Thalassia*. 10, 633 - 636.

Cardellicchio, N., Buccolieri, A., Giandomenico, S., Lopez, L., Pizzulli, F., Spada, L., 2007. Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian Sea, Southern Italy). *Marine Pollution Bulletin* 55, 451 – 458

Castro-Jimenez, J., Eisenreich, S. J., Ghiani, M., Mariani, G., Skejo, H., Umlauf, G., Wollgast, J., Zaldívar, J. M., Berrojalbiz, N., Dachs, J., Reuter, H. I., 2010. Atmospheric occurrence and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in the open Mediterranean Sea. *Environmental Science and Technology* 44, 5456 - 5463.

Chapman, P. M., Mann, G. S., 1999. Sediment quality values (SQVs) and ecological risk assessment (ERA). *Marine Pollution Bulletin* 38, 339 - 44.

Chu, W. K., Wong, M. H., Zhang, J., 2006. Accumulation, distribution and transformation of DDT and PCBs by *Phragmites australis* and *Oryza sativa* L.: I. Whole plant study. *Environmental Geochemistry and health* 28, 159 - 168.

Cousteau, J. Y., 1979. Rapport préliminaire de l'expédition C.I.E.S.M. Cousteau Society effectuée par le navire Calypso pour contribuer à l'établissement d'un "bulletin de Sante" de la Méditerranée. In: IP" Journ. Ces études Pollutions, Antalya, C.I.E.S.M., pp. 21-31.

Czuczwa, J., Leuenberger, C., Giger, W., 1988. Seasonal and temporal changes of organic compounds in rain and snow. *Atmospheric Environment* 22, 907 - 916.

Dachs, J., & Méjanelle, L., 2010. Organic pollutants in coastal waters, sediments, and biota: a relevant driver for ecosystems during the anthropocene. *Estuaries and Coasts* 33, 1-14.

Dachs, J., Bayona J.M., Fillaux J., Saliot A., and Albaigés J., 1999b. Evaluation of anthropogenic and biogenic inputs into the western Mediterranean using molecular markers. *Marine Chemistry* 65, 195 - 210.

Dachs, J., Eisenreich, S.J., 2000. Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons. *Environmental Science and Technology* 34, 3690 - 3697.

Dachs, J., Lohmann, R., Ockenden, W.A., Mejanelle, L., Eisenreich, S.J., Jones, K.C., 2002. Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. *Environmental Science and Technology* 36, 4229 - 4237.

De Luca, G., Furesi, A., Micera G., Panzanelli, A., Piu, P.C., Pilo, M.I., Spano, N., Sanna, G., 2005. Nature, distribution and origin of polycyclic aromatic hydrocarbons (PAHs) in the sediments of Olbia harbor (Northern Sardinia, Italy). *Marine Pollution Bulletin* 50, 1223–1232.

Derouiche, A., Sanda, Y. G., Driss, M. R., 2004. Polychlorinated biphenyls in sediments from Bizerte lagoon, Tunisia. *Bulletin of environmental contamination and toxicology* 73, 810 - 817.

Duinker, J.C., Schultz, D.E., Petrick, G. 1988. Selection of chlorinated biphenyl congeners for analysis in environmental samples. *Marine Pollution Bulletin* 19, 19-25.

Dvorská, A., Lammel, G., Klánová, J., 2011. Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe. *Atmospheric Environment* 45, 420 - 427.

ECETOC, 1988. Concentration of Industrial Organic Chemicals measured in the Environment: the Influence of Physico-Chemicals Properties, Tonnage and Use Pattern (Technical Report No. 29), European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels.

Elder, D. L. and Villeneuve, J. P., 1977b. Polychlorinated biphenyls in marine air, deep sediments and water of the Mediterranean Sea. *Thalassia Jugoslavica* 13, 59 - 62.

El-Dib, M. A., & Badawy, M. I. 1985. Organochlorine insecticides and PCBs in water, sediment, and fish from the Mediterranean Sea. *Bulletin of environmental contamination and toxicology*, 34(1), 216-227.

Eljarrat, E., Caixach, J., Rivera, J., de Torres, M., Ginebreda, A., 2001. Toxic potency assessment of non-and mono-ortho PCBs, PCDDs, PCDFs, and PAHs in northwest Mediterranean sediments (Catalonia, Spain). *Environmental science and technology* 35, 3589 - 3594.

Eljarrat, E., De La Cal, A., Larrazabal, D., Fabrellas, B., Fernandez-Alba, A.R., Borull, F., Marce, R.M., Barcelo, D., 2005. Occurrence of polybrominated diphenylethers, polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls in coastal sediments from Spain. *Environmental Pollution* 136, 493 - 501.

El-Shahawi, M. S., Hamza, A., Bashammakh, A. S., Al-Saggaf, W. T., 2010. An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants. *Talanta* 80, 1587 - 1597.

Fernández, M., Alonso, C., Hernández, LM., González, MJ., 1999 Occurrence of organochlorine insecticides, PCB and PCB congeners in waters and sediments of the Ebro River, Spain. *Chemosphere* 38, 33 - 43.

Fernandez, P. 1991. Caracterización biogeoquímica y ecotoxicológica de aportes orgánicos continentales en el litoral barcelonés. Ph Dissertation, Universidad de Barcelona, 405 p.

Fiedler, H., 2003. Dioxins and furans (PCDD/PCDF). In: Part O, Persistent Organic Pollutants. *The Handbook of Environmental Chemistry*, vol. 3. Springer Verlag, Berlin, Heidelberg, pp. 123 - 202.

Fiedler, H., 2003. *The Handbook of Environmental Chemistry, Persistent Organic Pollutants*, 3rd edn, Springer-Verlag, Berlin/Heidelberg, Chapter 1.

Fiedler, H., 2007. National PCDD/PCDF release inventories under the Stockholm Convention on Persistent Organic Pollutants. *Chemosphere* 67, S96 - S108.

Fignani, M., Bellucci, L.G., Favotto, M., Albertazzi, S., 2003. Polycyclic aromatic hydrocarbons in sediments of the Venice Lagoon. *Hydrobiologia* 494, 283 - 290.

Galanopoulou, S., Vgenopoulos, A., Conispoliatis, N., 2005. DDTs and other chlorinated organic pesticides and polychlorinated biphenyls pollution in the surface sediments of Keratsini harbour, Saronikos gulf, Greece. *Marine pollution bulletin* 50, 520 - 525.

Galiulin, R. V., Bashkin, V. N., Galiulina, R. A., 2002. Review: Behavior of persistent organic pollutants in the air-plant-soil system. *Water, Air, and Soil Pollution* 137, 179 - 191.

Garcia-Flor, N., Dachs J., Bayona J.M., and Albaigés J., 2009. Surface waters are a source of polychlorinated biphenyls to the coastal atmosphere of the north-western Mediterranean Sea. *Chemosphere* 75, 1144 - 1152.

Gardner, B., Hewitt, C.N., Jones, K.C., 1995. PAHs in air adjacent to two inland water bodies. *Environmental Science and Technology* 29, 2405 - 2413.

GESAMP, 1989. The Atmospheric Input of Trace Species to the World Ocean. WMO Reports and Studies No. 38, Joint Group of Experts on the Scientific Aspects of Marine Pollution, Geneva.

Geyer, H., Freitag, D. and Korte, F., 1984 Polychlorinated biphenyls (PCBs) in the marine environment, particularly in the Mediterranean. *Ecotoxicology and Environmental Safety*, 8, 129 -151.

Ghosh, U., Zimmerman, J. R., Luthy, R. G., 2003. PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. *Environmental science & technology* 37, 2209 - 2217.

Gobas, F.A.P.C., Wilcockson, J.B., Russell, R.W., Haffner, G.D., 1999. Mechanism of biomagnification in fish under laboratory and field conditions. *Environmental Science and Technology* 33, 133 - 141.

Gogou, A., Stratigakis, N., Kanakidou, M., Stephanou, E.G. ,1996. Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. *Organic Geochemistry* 25, 79 - 96.

Gómez-Gutiérrez, A., Garnacho, E., Bayona, J. M., Albaigés, J. 2007a. Assessment of the Mediterranean sediments contamination by persistent organic pollutants. *Environmental Pollution*, 148(2), 396-408.

Gómez-Gutiérrez, A., Garnacho, E., Bayona, J. M., Albaigés, J., 2007b. Screening ecological risk assessment of persistent organic pollutants in Mediterranean Sea sediments. *Environment International* 33, 867 - 876.

Grassi, P., Fattore, E., Generoso, C., Fanelli, R., Arvati, M., Zuccato, E., 2010. Polychlorobiphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in fruit and vegetables from an industrial area in northern Italy. *Chemosphere* 79, 292–298.

Grimalt, J., 1983. *Geoquímica orgánica de sistemas deltaicos*. PhD Dissertation, Barcelona, 330 pp.

Harvey, G. R., Steinhauer, W. G. and Teal, J. M. (1973) Polychlorobiphenyls in North Atlantic Ocean water. *Science* 180, 643 - 644.

Guerra, R. 2011. Polycyclic aromatic hydrocarbons, polychlorinated biphenyls and trace metals in sediments from a coastal lagoon (Northern Adriatic, Italy). *Water Air Soil Pollution* 223, 85 - 98.

Guzella, L., Rscioli, C., Vigano, L., Sarkar, S., Bhattacharya, A., 2005. *Environment International* 31, 523.

Hansen, J.C., 1998. The human health programme under AMAP. AMAP human health group. Arctic monitoring and assessment program. *International Journal of Circumpolar Health* 57, 280 - 291.

Harner, T., Pozo, K., Gouin, T., Macdonald, A. M., Hung, H., Caine, J., Peters, A., 2006. Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. *Environmental Pollution* 144, 445 - 452.

Harrad, S.J., Sewart, A.P., Alcock, R., Boumphrey, R., Burnett, V., Duartedavidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S.R., Jones, K.C., 1994. Polychlorinated-biphenyls (Pcbs) in the British environment e sinks, sources and temporal trends. *Environmental Pollution* 85, 131 - 146.

Hatzinger, P.B, Alexander, M., 1995. Effect of ageing chemicals in soil on their biodegradability and extractability. *Environmental Science and Technology* 29, 537- 545.

- Heintzenberg, J., 1989. Fine particles in the global troposphere: a review. *Tellus* 41B, 149 - 160.
- Holsen, T.M., Noll, K.E., Fang, G.-C., Lee, W.J., Lin, J.-M., Keeler, G.J. 1993. Dry deposition and particle size distributions measured during the Lake Michigan Urban Air Toxics study. *Environmental Science and Technology* 27, 1327 - 1333.
- Holsen, T.M., Noll, K.E., Liu, S.P., Lee, W.J. 1991. Dry deposition of polychlorinated biphenyls in urban areas. *Environmental Science and Technology* 25, 1075 - 1081.
- Hsu, Y.-K., Holsen, T.M., Hopke, P.K., 2003. Locating and quantifying PCB sources in Chicago: receptor modeling and field sampling. *Environmental Science and Technology* 37, 681 - 690.
- Hung, H., Lee, S.C., Wania, F., Blanchard, P., Brice, K., 2005b. Measuring and simulating atmospheric concentration trends of polychlorinated biphenyls in the Northern Hemisphere. *Atmospheric Environment* 39, 6502 - 6512.
- Jacquot, F., Le Dréau, Y., Doumenq, P., Munoz, D., Guiliano, M., Imbert, G., Mille, G., 1999. The origins of hydrocarbons trapped in the Lake of Berre sediments. *Chemosphere* 39, 1407 - 1419.
- Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., Jones, K.C., 2004c. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environmental Science and Technology* 38, 34 - 41.
- Jenkin, M.E. 1984. An investigation into the enhancement of deposition of hygroscopic aerosols to wet surfaces in a wind tunnel. *Atmospheric Environment* 18, 1017 - 1024.
- Jeremiason, J.D., Hornbuckle, K.C., Eisenreich, S.J., 1994. Pcb's in Lake-Superior, 1978 - 1992: decreases in water concentrations reflect loss by volatilization. *Environmental Science and Technology* 28, 903 - 914.
- Jones, K. C., De Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. *Environmental pollution* 100, 209 - 221.
- Jurado, E., Lohmann R., Meijer S., Jones K.C., and Dachs J., 2004. Latitudinal and seasonal capacity of the surface ocean as a reservoir of polychlorinated biphenyls. *Environmental Pollution* 128, 149-162.
- Kanzari, F., Syakti, A. D., Asia, L., Malleret, L., Mille, G., Jamoussi, B., Doumenq, P., 2012. Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine, and organophosphorous pesticides in surface sediments from the Arc river and the Berre lagoon, France. *Environmental Science and Pollution Research* 19, 559 - 576.
- Kavouras, I.G., Stephanou, E.G. 2002. Gas/Particle partitioning and size distribution of Primary and Secondary carbonaceous aerosols in Public Buildings. *Indoor Air* 12, 17 - 32.
- Kelce, W. R., Stone, C. R., Laws, S. C., Gray, L. E., Kemppainen, J. A., Wilson, E. M., 1995. Persistent DDT metabolite p,p'DDE is a potent androgen receptor antagonist.
- Kilikidis, S., Kamarianos, A., Karamanlis, X., Gianakou, U., 1994. Determination of polycyclic aromatic hydrocarbons in the effluents of an urban waste treatment plant and the water, sediments and mussels of the receiver Thermaikos Gulf (N. Greece). *Fresenius Environmental Bulletin* 3, 293 - 299.
- Koci, K., 1998. The trend of POP pollution in the Albanian Adriatic Coast. *Case Study PCBs (1992-1996)*. UNEP/IFCS, pp. 101 - 106.
- Korytár, P., Leonards, P. E. G., De Boer, J., Brinkman, U. T., 2002. High-resolution separation of polychlorinated biphenyls by comprehensive two-dimensional gas chromatography. *Journal of Chromatography A* 958, 203 - 218.
- La Rocca, C., Conti, L., Crebelli, R., Crochi, B., Iacovella, N., Rodriguez, F., Turrio Baldassarri, L., Di Domenico, A., 1996. PAHs content and mutagenicity of marine

sediments from the Venice lagoon. *Ecotoxicology and Environmental Safety* 33, 236 - 245.

Larsson, P., Andersson, A., Broman, D., Nordbäck, J., Lundberg, E., 2000. Persistent organic pollutants (POPs) in pelagic systems. *Ambio* 29, 202 - 209.

Lecouffe, LC., 1986. Etat actuel de la pollution sur les fonds du secteur de Cortiou (Marseille). Thèse de Pharmacie, Aix-Marseille II, pp. 1 – 47.

Li, Y. F., Macdonald, R. W., 2005. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. *The Science of the Total Environment* 342, 87 - 106.

Lipiatou, E., Saliot, A., 1991 Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the Western Mediterranean Sea. *Marine Chemistry* 32, 51 - 71.

Loganathan, G.B., Kannan, K., 1994. Global organochlorine contamination trends: an overview. *Ambio* 23, 187 - 190.

Lohmann, R., Breivik, K., Dachs, J., Muir, D., 2007. Global fate of POPs: Current and future research trends. *Environmental Pollution* 150, 150 - 186.

Lohmann, R., Lammel, G., 2004. Adsorptive and absorptive contributions to the gas-particle partitioning of polycyclic aromatic hydrocarbons: state of knowledge and recommended parametrization for modeling. *Environmental Science and Technology* 38, 3793 - 3803.

Louiz, I., Kinani, S., Gouze, M.E., Ben-Attia, M., Menif, D., Bouchonnet, S., Porcher, J.M., Ben-Hassine, O.K., Aït-Aïssa, S., 2008. Monitoring of dioxin-like, estrogenic and anti-androgenic activities in sediments of the Bizerta lagoon (Tunisia) by means of in vitro cell-based bioassays: Contribution of low concentrations of polynuclear aromatic hydrocarbons (PAHs). *Science of Total Environment* 402, 318 - 329.

Mackay, D., Wania, F., 1995. Transport of contaminants to the Arctic: partitioning, processes and models. *The Science of the Total Environment* 160/161, 25 - 38.

Martínez-Lladó, X., Gibert, O., Martí, V., Díez, S., Romo, J., Bayona, J. M., de Pablo, J., 2007. Distribution of polycyclic aromatic hydrocarbons (PAHs) and tributyltin (TBT) in Barcelona harbour sediments and their impact on benthic communities. *Environmental Pollution* 149, 104 - 113.

McVeety, B.D., Hites, R.A., 1988. Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. *Atmospheric Environment* 22, 511- 536.

Merhaby, D., Net, S., Rabodonirina, S., Ouddane, B., Halwani, J., 2015b. Assessment of organic pollutants in surficial sediments along Lebanese coastal zone. Submitted paper.

Mostafa, A.R., Barakat, A.O., Qian, Y., Wade, T.L., 2003. Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the western harbour of Alexandria, Egypt. *J. Soils Sediments* 3, 173 - 179.

Muir, D.C.G., Howard P.H., 2006. Are there new persistent organic pollutants? A challenge for environmental chemists. *Environmental Science and Technology* 40, 7157–7166.

Officer, C.B., 1981. Physical dynamics of estuarine suspended sediments. *Marine Geology* 40, 1-14.

Okay, O. S., Karacık, B., Başak, S., Henkelmann, B., Bernhöft, S., Schramm, K. W., 2009. PCB and PCDD/F in sediments and mussels of the Istanbul strait (Turkey). *Chemosphere*, 76, 159 - 166.

Ozcan, S., Tor, A., Aydin, M.E., 2009. Application of ultrasound-assisted emulsification-microextraction for the analysis of organochlorine pesticides in waters, *Water Research* 43, 4269 - 4277.

Pankow, J.F., 1994a. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment* 28, 185 - 188.

Pankow, J.F., 1994b. An absorption model of gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmospheric Environment* 28, 189 - 193.

Parolini, M., Bellucci, L.G., Carraro, C., Raccanelli, S., 2001. Polychlorinated biphenyls in sediments of the Venice Lagoon. *Chemosphere* 43, 567 - 575.

Parolini, M., Binelli, A., Matozzo, V., Marin, M.G., 2010. Persistent organic pollutants in sediments from the Lagoon of Venice—a possible hazard for sedimentdwelling organisms. *J. Soils Sedim.* 10, 1362 - 1379.

Pavoni, B., Mecozzi, M., Berto, D., Ausili, A., Romano, E., Amici, M., Zharova, N., Amato, E., 2003. Micropollutants, organic carbon and textural properties in surface sediments in the Moroccan coast near AlHoceïma. *Toxicological Environmental Chemistry* 84, 53 - 67.

Piaggi, S., Novelli, M., Martino, L., Masini, M., Orciuolo, C.R.E., Masiello, P., Casini, A., De Tata, V., 2007. Cell death and impairment of glucose-stimulated insulin secretion induced 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in the β -cell line INS-1E. *Toxicology and Applied Pharmacology* 220, 333 - 340.

Picer, N., Picer, M., 1992. Inflow, levels and the fate of some persistent chlorinated hydrocarbons in the Rijeka Bay area of the Adriatic Sea. *Water Res.* 26, 899–909.

Picer, M., Picer, A., Nazansky, B., 1981. Persistent chlorinated hydrocarbons in the Rijeka Bay. *Thal. Jugosl.* 17, 225 - 236.

Pirrone, N., Keeler, G.J., Holsen, T.M., 1995. Dry deposition of semivolatile organic compounds to Lake Michigan. *Environmental Science and Technology* 29, 2123 - 2132.

Pistikopoulos, P., Wortham, H.M., Gomes, L., Masclet-Beyne, S., Bon Nguyen, E., Masclet, P.A., Mouvier, G., 1990. Mechanisms of formation of particulate polycyclic hydrocarbons in relation to the particle size distribution; effects on meso-scale transport. *Atmospheric Environment* 24A, 2573 - 2584.

Pitta, P., Giannakourou, A., Christaki, U., 2001. Planktonic ciliates in the oligotrophic Mediterranean Sea: longitudinal trends of standing stocks, distributions and analysis of food vacuole contents. *Aquatic Microbial Ecology* 24, 297 - 311.

Puccetti, G., Leoni, V., 1980. PCB and HCB in the sediments and waters of the Tiber estuary. *Marine Pollution Bulletin* 11, 22 - 25.

Restrepo, B.J., Kannan, K., Addink R., Adams, D.H., 2005. Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. *Environmental Science and Technology* 39, 8243 - 8250.

Robson, M., Harrad, S.J., 2004. Chiral PCB signatures in air and soil: Implications for atmospheric source apportionment. *Environmental Science and Technology* 38, 1662 - 1666.

Schwarzenbach, R., Imboden, D., and Pschwend P., 2003. *Environmental Organic Chemistry*. New York: Wiley.

Schwarzenbach, R.E., Gschwend, P.M., Imboden, D.M., 1993. *Environmental Organic Chemistry*. John Wiley, New York.

Secco, T., Pelizzato, F., Sfriso, A., Pavoni, B., 2005. The changing state of contamination in the Lagoon of Venice. Part 1: organic pollutants. *Chemosphere* 58, 279 - 290.

Shao, C. 2001. Status and Prevention Strategies of PCBs in China. *Memoirs of Seminar on Persistent Organic Pollutants*, SEPA, Beijing, 70 pp.

Sicre, M.A., Marty, J.C., Saliot, A., Aparicio, X., Grimalt, J., Albaige's, J., 1987. Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin. *Atmospheric Environment* 21, 2247 - 2259.

Slobodnik, J. Results of the world's biggest river expedition. WELCOME TO ISSUE N 4.

Sprovieri, M., Feo, M.L., Prevedello, L., Salvagio Manta, D., Sammartino, S., Tamburrino, S., Marsella, E., 2007. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere* 67, 998 - 1009.

Strukov, B. (2006). Modelling of global POPs distribution in the sea environment. EMEP/MSC-E Technical Report 7.

Suess, M. J., 1976. The environmental load and cycle of polycyclic aromatic hydrocarbons. *The Science of the Total Environment* 6, 239 - 250.

Tasdemir, Y., Esen, F., 2007. Urban air PAHs: concentrations, temporal changes and gas/particle partitioning at a traffic site in Turkey. *Atmospheric Research* 84, 1 e12.

Telli-Karakoç, F., Tolun, L., Henkelmann, B., Klimm, C., Okay, O., Schramm, K. W., 2002. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) distributions in the Bay of Marmara sea: Izmit Bay. *Environmental Pollution*, 119, 383 - 397.

Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution* 162, 110-119.

Tolosa, I., Bayona, J.M., Albaigés, J., 1995. Spatial and temporal distribution, fluxes, and budgets of organochlorinated compounds in northwest Mediterranean sediments. *Environmental Science and Technology* 29, 2519 - 2527.

Tolosa, I., Bayona, J.M., Albaigés, J., 1996. Aliphatic and polycyclic aromatic hydrocarbons and sulphur/oxygen derivatives in northwestern Mediterranean sediments: Spatial and temporal variability, fluxes and budgets. *Environmental Science Technology* 30, 2495 - 2503.

Tolun, L.G., Okay, O.S., Grains, A .F., Tolay, M., Tüfekci, H., Kiratli, N., 2001. The pollution status and the toxicity of surface sediments in Izmit Bay (Marmara Sea), Turkey. *Environ. Interpret.* 26, 163 – 168.

Trabelsi, S., Driss, MR., 2005 Polycyclic aromatic hydrocarbons in superficial coastal sediments from Bizerte Lagoon, Tunisia. *Marine Pollution Bulletin* 50, 344 - 359.

Turley, C. M., Bianchi, M., Christaki, U., Conan, P., Harris, J. R. W., Psarra, S., Ruddy, G., Stutt, E. D., Tselepidis, A., Van Wambeke, F., 2000. Relationship between primary producers and bacteria in an oligotrophic sea - the Mediterranean and biogeochemical implications. *Marine Ecological Progress Series* 193, 11 - 18.

UNECE, 1998. The 1998 Aarhus Protocol on Persistent Organic Pollutants (POPs). Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants. United Nations Economic Commission for Europe. http://www.unece.org/env/lrtap/pops_h1.htm.

UNECE, 1998a. Draft Protocol to the Convention on Long-range Air Pollution on Persistent Organic Pollutants, (EB.AIR/1998/2), Convention on Long-range Transboundary Air Pollution, United Nations Economic and Social Council, Economic Commission for Europe.

UNEP, 1999. UNEP Chemicals: Dioxin and Furan Inventories - National and Regional Emissions of PCDD/Fs. United Nations Environment Programme.

UNEP, 2001. Final Act of the Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants. United Nations Environment Program Chemicals, Geneva, Switzerland. 445.

UNEP, 2002. Regionally Based Assessment of Persistent Toxic Substances. Mediterranean Regional Report, UNEP, Switzerland.

UNEP, 2003. Regionally Based Assessment of Persistent Toxic Substances. Global Report, UNEP, Switzerland.

UNEP, 2005. Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, second ed. United Nations Environment Programme Chemicals, Geneva, Switzerland. Available from: <http://www.pops.int/>.

UNEP/MAP, 1999a Strategic action programme to address pollution from land-based activities. MAP technical reports series, vol. 119. Athens, Greece: UNEP;1999a.

UNEP/MAP, 2001. Protecting the Mediterranean from Land/Based Pollution, UNEP, Athens.

UNEP/MAP. MEDPOL Phase III. Programme for the assessment and control of pollution in the Mediterranean region. MAP technical series. Athens, Greece: UNEP; 1999b.

UNIDO, 2000. Presented at the ICS, UNIDO Workshop on Contamination of Food and Agro Products, Croatia.

United Nations Environment Programme (UNEP)., 1999. Inventory of information source on chemicals-persistent organic pollutants. Geneva, Switzerland. chemicals, November.

Ünlü, S., Alpar, B., 2006. Distribution and sources of hydrocarbons in surface sediments of Gemlik Bay (Marmara Sea, Turkey). *Chemosphere* 64, 764 - 777.

Uraki, Y., Suzuki, S., Yasuhara, A., Shibamoto, T., 2004. Determining source of atmospheric polychlorinated biphenyls based on their fracturing concentrations and congener compositions. *Journal of Environmental Science and Health, Part A* 39, 2755 - 2772.

USEPA., 1998. Guidelines for ecological risk assessment. Washington, DC: US Environmental Protection Agency, EPA/630/R-95/002F.

Vallack, H. W., Bakker, D. J., Brandt, I., Broström-Lundén, E., Brouwer, A., Bull, K. R., Taalman, R. D., 1998. Controlling persistent organic pollutants—what next. *Environmental Toxicology and Pharmacology* 6, 143 - 175.

Van Oostdam, J., Donaldson, S.G., Feeley, M., Arnold, D., Ayotte, P., Bondy, G., Chan, L., Dewailly, E., Furgal, C.M., Kuhnlein, H., Loring, E., Muckle, G., Myles, E., Receveur, O., Tracy, B., Gill, U., Kalhok, S., 2005. Human health implications of environmental contaminants in Arctic Canada: a review. *Science of the Total Environment*, 351 - 352, 165 - 246.

Van Vaeck, L., Van Cauwenberghe, K.A., 1978. Cascade impactor measurements of the size distribution of the major classes of organic pollutants in atmospheric particulate matter. *Atmospheric Environment* 12, 2229 - 2239.

Vassura, I., Foschini, F., Baravelli, V., Fabbri, D., 2005. Distribution of alternant and non-alternant polycyclic aromatic hydrocarbons in sediments and clams of the Pialassa Baiona Lagoon (Ravenna, Italy). *Chemical Ecology* 21, 1 - 10.

Venkataraman, C., Friedlander, S.H., 1994. Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 2. Ambient measurements and effects of atmospheric processes. *Environmental Science and Technology* 28, 563 - 572.

Vestreng, V., Rigler, E., Adams, M., Kindbom, K., Pacyna, J.M., Denier van der Gon, H.D., Reis, S., Travnikov, O., 2006. Inventory Review. Emission data reported to the LRTAP Convention and NEC Directive. EMEP Technical Report MSC-W 1/2006. 130 pp. (ISSN 1504 - 6179, see also <http://webdab.emep.int>).

Viganò, L., Arillo, A., Buffagni, A., Camusso, M., Ciannarella, R., Crosa, G., Falugi, C., Galassi, S., Guzzella, L., Lopez, A., Mingazzini, M., Pagnotta, R., Patrolecco, L., Tartari, G., Valsecchi, S., 2003. Quality assessment of bed sediments of the Po River (Italy). *Water Research* 37, 501 - 518.

Villa, S., Finizio, A., Diaz, R. D., Vighi, M., 2003. Distribution of organochlorine pesticides in pine needles of an oceanic island: the case of Tenerife (Canary Islands, Spain). *Water, Air, and Soil Pollution* 146, 335 - 349.

- Voldner, E.C., Li, Y. F., 1993. Global usage of toxaphene. *Chemosphere* 27, 2073 - 2078.
- Wallberg, P., Andersson, A., 2000. Transfer of carbon and polychlorinated biphenyl through the pelagic microbial food web in a coastal ecosystem. *Environmental Toxicology and Chemistry* 18, 1250 - 1257.
- Wang, Z.D., Fingas, M., Shu, Y.Y., Sigouin, L., Landriault, M., Lambert, P., Turpin, R., Campagna, P., Mullin, J. 1999. Quantitative characterization of PAHs in burn residue and soot samples and differentiation of pyrogenic PAHs from petrogenic PAHs – the 1994 mobile burn study. *Environmental Science and Technology* 33, 3100 - 3109.
- Wania, F., 2003. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in Polar Regions. *Environmental Science and Technology* 37, 1344 - 1351.
- Wania, F., 2006. Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic. *Environmental Science and Technology* 40, 569- 577.
- Wania, F., Axelman, J., & Broman, D., 1998. A review of processes involved in the exchange of persistent organic pollutants across the air–sea interface. *Environmental Pollution* 102, 3 - 23.
- Yamashita, N., Urushigawa, Y., Masunaga, S., Walash, M.I., Miyazaki, A., 2000. Organochlorine pesticides in water, sediment and fish from the Nile River and Manzala Lake in Egypt. *International Journal of Environmental and Analytical Chemistry* 77, 289 – 303.
- Yan, S., Rodenburg L.A., Dachs J., and Eisenreich S.J., 2008. Seasonal air-water exchange fluxes of polychlorinated biphenyls in the Hudson River estuary. *Environmental Pollution* 152, 443 - 452.
- Yang, X. 1989. Pesticides and Environment. *Pestic. Sci. Manage.* 1989 (1) (in Chinese).
- Yao, E., Zhang, G. 2001. Some POPs Conventions with Relevance to their Production and Application in China. *Memoirs of Seminar on Persistent Organic Pollutants*, State Environmental Protection Administration of China (SEPA), Beijing, 76 pp.
- Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic geochemistry* 33, 489 - 515.
- Zaghden, H., Kallel, M., Elleuch, B., Oudot, J., and Saliot, A., 2007. Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Sfax, Tunisia, Mediterranean Sea. *Marine Chemistry* 105, 70 - 89.
- Zhang, H., Lu, Y., Shi, Y., Wang, T., Xing, Y., Dawson, R. W., 2005. Legal framework related to persistent organic pollutants (POPs) management in China. *Environmental Science & Policy* 8, 153 - 160.
- Zhang, P., Song, J., Yuan, H., 2009. Persistent organic pollutant residues in the sediments and mollusks from the Bohai Sea coastal areas, North China: an overview. *Environment international*, 35, 632 - 646.
- Zhao, X., Zheng, B., Qin, Y., Jiao, L., Zhang, L., 2010. Grain size effect on PBDE and PCB concentrations in sediments from the intertidal zone of Bohai Bay, China. *Chemosphere* 81, 1022 - 1026.

Tables and figures

Table 1 Legacy POPs controlled under Stockholm convention (UNEP, 2001), CLRTAP POPs protocol (substances also specified in UNEP Governing Council Decision 19/13c for initial inclusion in the global POPs convention are shown in bold type) (UNEP, 2001).

Chemicals	Period of emissions estimates	Cumulative global production or annual Emissions (Kt)	References (31)
<i>Organochlorine Pesticides</i>			
Aldrin ^a			
Chordane ^a			
Chlorodecone ^{a,d}			
DDT ^{a,b}	1940s-present	4500 kt	Li and Macdonald (2005)
Dieldrin ^a			
Endrin ^a			
Heptachlor ^a			
Hexachlorobenzene (HCB) ^{a,c}	~ 1995	~ 23t/year	Bailey (2001)
Hexachlorocyclohexane (HCH) ^{a,b,d}			
Mirex ^a			
Toxaphene ^a	1950-1993	1330 kt	Voldner and Li (1993) see also Li and Macdonald (2005)
<i>Industrial products</i>			
Hexabromobophenyl ^{a,d}			
Polychlorinated biphenyls (PCBs) ^{a,b}	1930-1993	1326 kt	Breivik et al. (2007)
<i>Unintentional by-products of combustion and industrial processes</i>			
Polycyclic aromatic hydrocarbons (PAHs) ^{c,d,e}	1966-1969	5000 t/year	Suess (1976)
Polychlorinated dibenzo-p-dioxins (PCDDs) ^c	~ 1995	9.9 kg TEQ/year	UNEP (1999); Fiedler (2003)
Polychlorinated dibenzofurans (PCDFs) ^c	~ 1995		

^a Listed under Annex I of the protocol (substances scheduled for elimination).

^b Listed under Annex II of the protocol (substances scheduled for restriction on use).

^c Listed under Annex III of the protocol (substances scheduled for emission reductions by the use of BAT (best available technology)).

^d Only Regulated under the Aarhus Protocol on POPs (UNECE, 1998).

^e Data emissions refers to B[a]P only (Suess, 1976).

Table 2 Some PAHs diagnostic ratios used for discrimination between petroleum and combustion sources

(A) Ratios	Petroleum	Mixed sources	Combustion		References
LMW/HMW	>1	-	<1	Grass, Wood and coal	Sicre et al., 1987 Budzinski et al., 1997 Cardellicchio et al., 2007
Phe/Ant	>10		<10		Baumard et al., 1999
Flu/Pyr	<1		>1		Baumard et al., 1999
Flu/Flu+Pyr	<0.4	0.4-0.5	>0.5	Grass, Wood and coal	Yunker et al. 2002
Ant/Ant+Phe	<0.1	-	>0.1	Combustion	Yunker et al., 2002
BaA/ (BaA+Chr)	<0.2	0.2-0.35	>0.35	Combustion	Yunker et al., 2002
IP/ IP+BghiP	<0.2	0.2-0.5	>0.5	Grass, Wood and coal	Wang et al., 1999 Yunker et al. 2002
Flu/Pyr	<1	-	>1		Baumard et al., 1998 De Luca et al., 2005
1,7/2,6+1,7-DMP			<0.45	Vehicle emissions	Yunker et al., 2002
			0.45-0.7	Mixed sources	Yunker et al., 2002
			>0.7	Wood combustion	Yunker et al., 2002
C0 / (C0+C1) F/P	<0.5	-	>0.5	Combustion	Yunker et al., 2002
C0 / (C0+C1) P/A	<0.5*	-	>0.5	Combustion	Yunker et al., 2002

*Petroleum or Combustion

Table 1 Highest total concentrations of Σ PAHs ($\mu\text{g}\cdot\text{kg}^{-1}$ d.w.) found in sediment samples collected from Mediterranean sites

<i>Studied sites</i>	<i>Min. Concentration</i>	<i>Max. Concentration</i>	<i>N° PAHs</i>	<i>References</i>
Italy				
<i>Naples harbour</i>	9	31774	16	Sprovieri et al., 2007
<i>Venice Lagoon</i>	65	48000		La Rocca et al., 1996
<i>Venice Lagoon</i>	315	810		Frignani et al., 2003
<i>Venice Lagoon</i>	15.1	388.9		Parolini et al., 2010
<i>Venice Lagoon</i>	20	502		Secco et al., 2005
<i>Pialassa Baiona</i>	1000	135000		Vassura et al. (2005)
<i>Pialassa Baiona</i>	3030	87150		Guerra., 2011)
<i>Mar Piccolo, Taranto</i>	380	12750	16	Cardellicchio et al., 2007

<i>Mar Piccolo, Taranto</i>	100	180		Cardellicchio et al., 1989
<i>Gulf of Taranto</i>	1484	262446	16	Annicchiarico et al., 2011
<i>Po River</i>	100	1800		Viganò et al., 2003
		France		
<i>Ajaccio harbour, Corse</i>		20440	26	Baumard et al., 1998a
<i>Lazaret Bay</i>	1440	48090	14	Benlahcen et al., 1997
<i>Lazaret navy harbour</i>		13010	14	Baumard et al., 1998a
<i>Gulf of Lions</i>	80.00	1500.00	11	Tolosa et al., 1996
<i>Gulf of Lions</i>	161.00	2176.00	21	Bouloubassi et al., 2012
<i>Berre Lagoon</i>	38	2323		Jacquot et al., 1999
<i>Berre lagoon</i>	334	853	16	Kanzari et al., 2012
<i>Thau Lagoon</i>	59	7679		Leaute., 2008
<i>Rhone Delta</i>	325	3182		Lipiatou and Saliot., 1991
<i>Rhone River</i>	1070	6330	15	Bouloubassi and Saliot., 1993
<i>Gironde Estuary</i>	18.5	4888	17	Budzinski et al., 1997
		Spain		
<i>Barcelona harbour</i>	1740	8420		Baumard et al., 1998b
<i>Barcelona harbour</i>	300	10320	16	Martínez-Lladó et al., 2007
<i>Besós River</i>		1299		Eljarrat et al., 2001
<i>Francofí River</i>		3050		Eljarrat et al., 2001
<i>Llobregat River</i>		3650		Eljarrat et al., 2001
		Greece		
<i>Thermaikos Gulf</i>	580	930		Kilikidis et al., 1994
		Morocco		
<i>Moroccan Coast</i>	15	551	16	Pavoni et al., 2003
		Turkey		
<i>Izmit Bay</i>	2500	25,000	14	Tolun et al. 2001
<i>Izmit Bay</i>	30000	1670000		Telli-Karakoç et al., 2002
<i>Gemlik Bay, Turkey</i>	50.8	13482	13	Ünlü and Alpar., 2006
		Egypt		
<i>Alexandria Harbour</i>	8	131150	43	Mostafa et al., 2003
<i>Alexandria Harbour</i>	180	14100		Barakat et al., 2011
<i>Nile Rive</i>	305	933		Badawy and Emababy., 2010
		Tunisia		
<i>Sfax–Kerkennah coastal zone</i>	113	10720	10	Zaghden et al., 2007
<i>Bizerte Lagoon</i>	83.3	447.1		Trabelsi and Driss., 2005
<i>Bizerta Lagoon</i>	1.5	2500		Louiz et al., 2008

		Slovenia		
ŠKocjan		1026		Bajt., 2008
		Croatia		
Rovinj area	32	13681	16	Bihari et al., 2006
Rijeka Bay	53	12532		Alebic-Juretic., 2011
		Lebanon		
Port of Beirut		3772.6	16	Merhaby et al., 2015b
Abou Ali Estuary		667.8	16	Merhaby et al., 2015b

Table 2 Total concentrations of Σ PCBs ($\mu\text{g}\cdot\text{kg}^{-1}$ d.w.) found in sediments collected from Mediterranean sites

Sites	Min. Concentration	Max. Concentration	N°CB	References
		Italy		
Naples harbour	1	899	38	Sprovieri et al., 2007
Gulf of Taranto	85	1780		Annicchiarico et al., 2011
Naples Bay	6	3200		Baldi et al., 1983
Venice Lagoon	6	1590		Frignani et al. 2001
Mar Piccolo, Taranto	2	1684		Cardellicchio et al., 2007
Tiber River	28	770		Puccetti and Leoni., 1980
Provencal basin, open sea	2	3		Tolosa et al., 1995
Tyrrhenian Sea	0.8	1.3		Geyer et al., 1984
North Adriatic	3.2	58		Burns and Villeneuve., 1983,1985
		France		
Cortiou, Marseille	5503	22900		Lecouffe., 1986
Rhone estuary	159	416		Tolosa et al., 1995
Arc River	0.3	467	7	Kanzari et al., 2012
Berre Lagoon	468.8	541.4	7	Kanzari et al., 2012
		Greece		
Keratsini harbour	4.78	351.8	11	Galanopoulou et al., 2005
		Spain		
Barcelona Coast	4	654		Fernandez, 1991
Catalan Coast (10 Rivers)	1.1	311		Eljarrat et al., 2001
Ebro River	5.3	1,772		Fernández et al., 1999
Ebro estuary	1	410		Grimalt, 1983
Catalan basin, open sea	4	11		Tolosa et al., 1995
		Egypt		
Alexendria Harbour	0.9	1211		Barakat et al., 2002
Port-Said	53	1500		El-Dib et., 1985
Manzala Lake	125	330		Yamashita et al., 2000
		Turkey		
Istanbul strait	0.179	539.746	18	Okay et al., 2009
		Tunisia		
Bizerte Lagoon	0.89	6.63	20	Derouiche et al., 2004
		Algeria		

Algerian Coast (Alger and Oran)	7	323		Cousteau., 1979
Algerian margin, open sea		9		Elder and Villeneuve., 1977b
Rijeka Bay, coast	0.9	Croatia 597		Picer et al., 1981 Picer and Picer., 1992)
Adriatic coast	1	Albany 5		Koci., 1998
Port of Beirut		Lebanon 1303	28	Merhaby et al., 2015b
Port of Jiyeh		718.2	28	Merhaby et al., 2015b
Abou Ali Estuary		339.4	28	Merhaby et al., 2015b

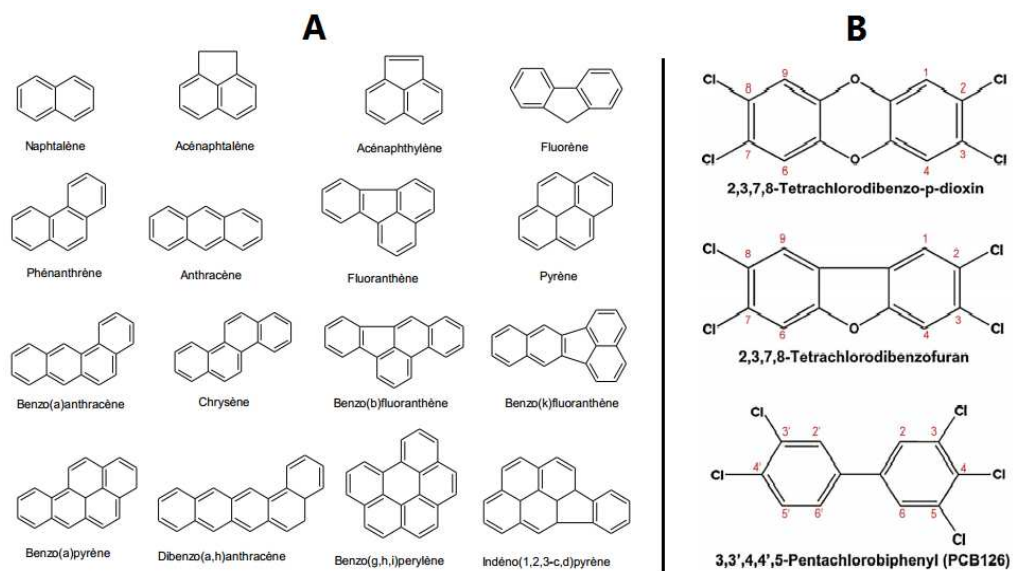


Figure 1 A: Structure of 16 PAHs listed as priority compounds in the U.S. EPA and B: basic structures of polychlorinated biphenyls (PCBs), chlorinated dibenzofurans (furans) and Chlorinated dibenzo-p-dioxins.

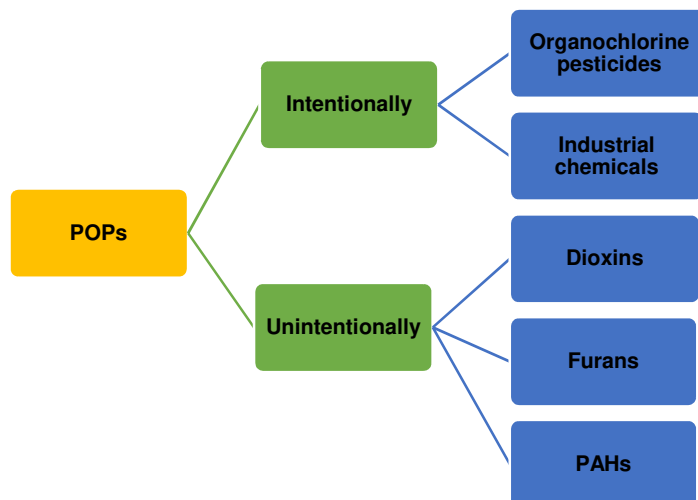


Figure 2 POPs classification

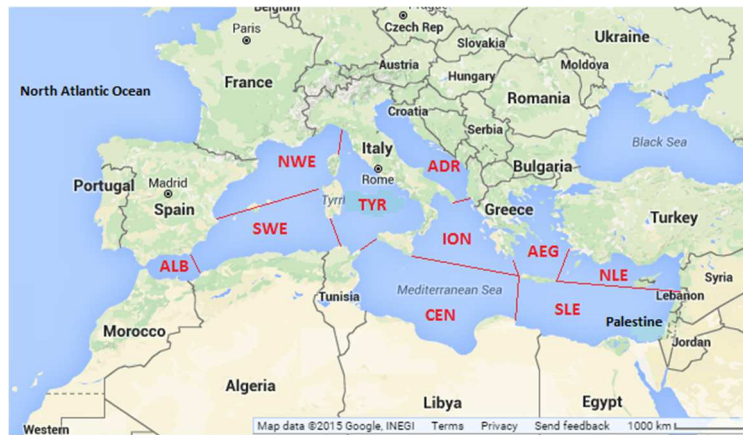


Figure 1 Location of sampling points in the Mediterranean Sea. The Mediterranean sub-basins are indicated as follows: ADR, Adriatic Sea; CEN, Central Sea; AEG, Aegean Sea; ALB, Alboran Sea; ION, Ionian Sea; NLE, North Levantine Sea; NWE, Northwestern Med

Figure 3 source: <https://www.google.com/maps/place/Mer+M%C3%A9diterran%C3%A9e/@36.6223748,-2.9445746,4z/data=!3m1!4b1!4m5!3m4!1s0x131421b81c473c9f:0x2e93598afeccf840!8m2!3d34.5531284!4d18.0480105>

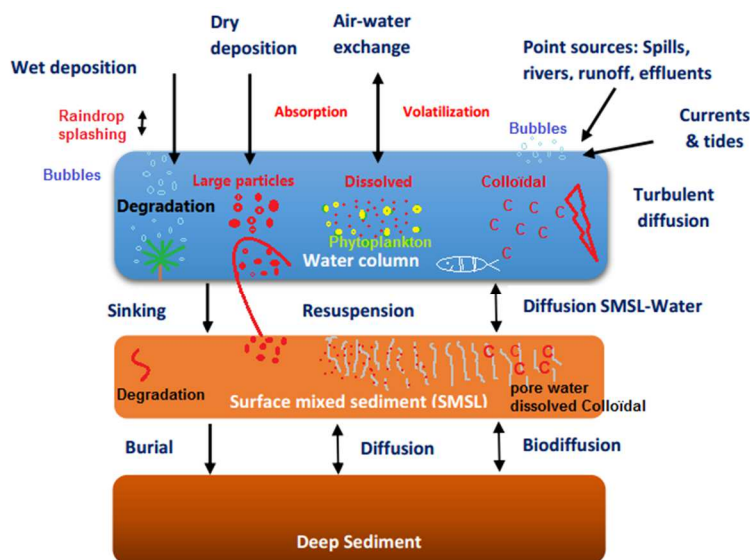


Figure 4 Schematics of the processes driving the environmental fate of POPs in coastal waters (modified Dachs and Méjanelle, 2010)

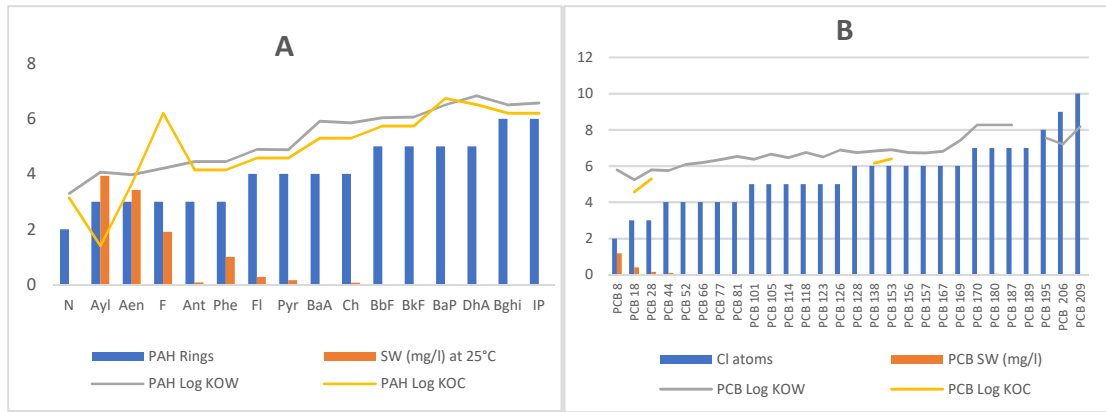


Figure 5 The Variation of the water solubility (S_w), Octanol-water and Octanol-particulate carbon partitioning coefficient (Log K_{ow} and Log K_{oc}) partitioning coefficient for some POPs (PAHs and PCBs) according to numbers of (A) PAHs rings and (B) PCBs Chlorine atoms.

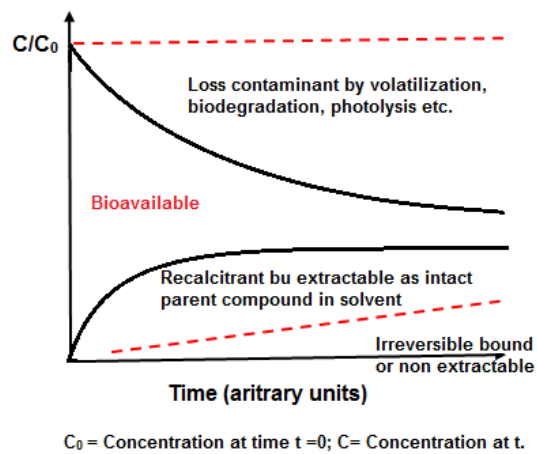


Figure 2 Conceptual graph of the possible forms of POPs in soil and sediment (Jones et al., 1999)

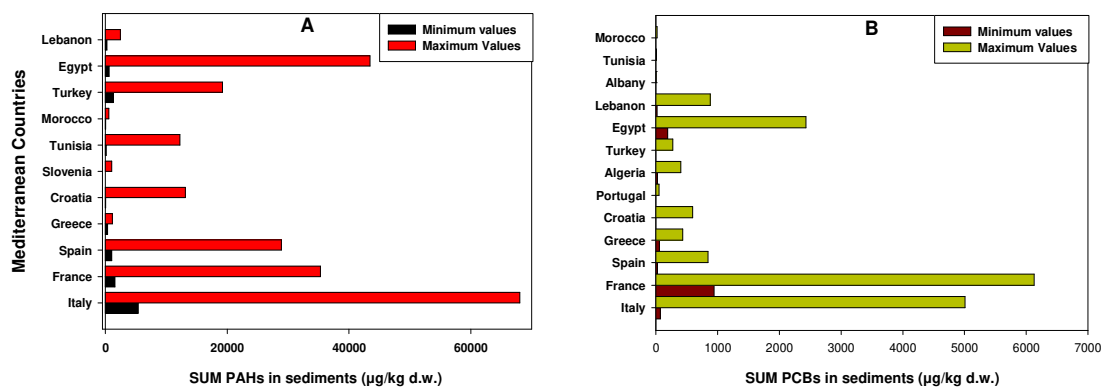


Figure 3 The total means concentrations of PAHs (A) and PCBs (B) in sediments for each Mediterranean country

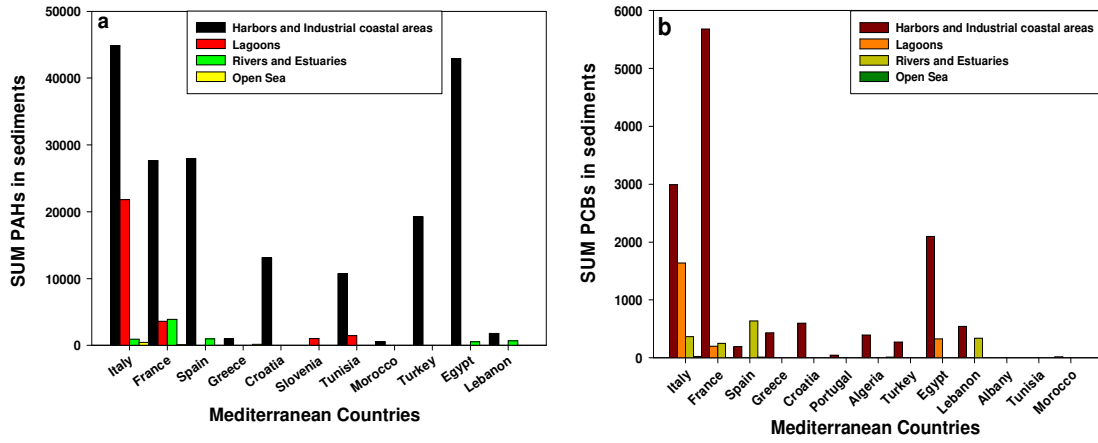


Figure 4 Total mean concentrations of the Σ_{10-26} PAHs and Σ_{7-41} PCBs in sediments for each Mediterranean country for the four categories

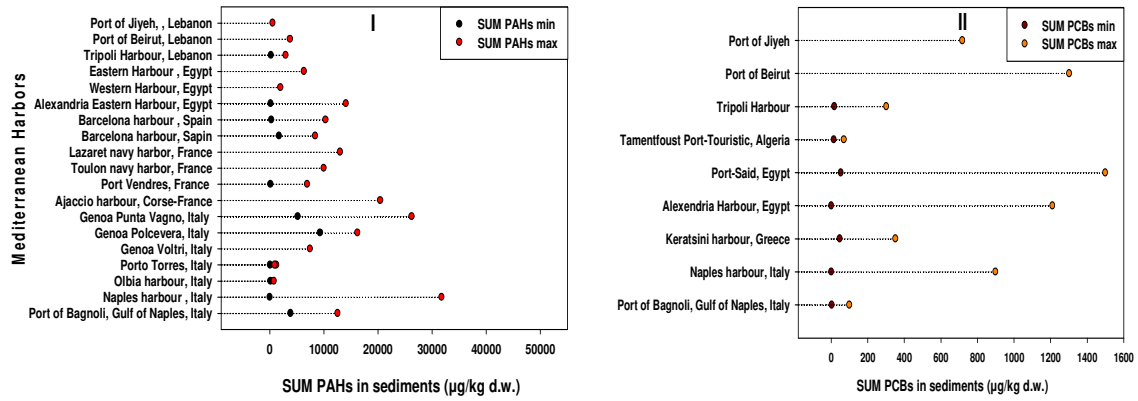


Figure 5 Concentration of Σ PAHs (I) and Σ PCBs (II) in sediment harbors of some Mediterranean countries

Mediterranean Sea

