N ° d'ordre: 41952

THÈSE

Présentée à

L'UNIVERSITÉ DE LILLE, SCIENCES ET TECHNOLOGIES

ECOLE DOCTORALE DES SCIENCES DE LA MATIÈRE, DE RAYONNEMENT ET DE L'ENVIRONNEMENT

Pour obtenir le grade de
DOCTEUR
Spécialité : Optique, Lasers, Physico-chimie, Atmosphère

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CARACTERISATION DE LA POLLUTION ORGANIQUE ET INORGANIQUE DANS LES SEDIMENTS PORTUAIRES DU LIBAN

CHARACTERIZATION OF ORGANIC AND INORGANIC POLLUTION IN LEBANON PORTS SEDIMENT

Soutenue le 14 Décembre 2015 devant le Jury composé de :

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REMERCIEMENTS

Ce travail de thèse a été réalisé principalement à L'université Lille 1, au sein du Laboratoire de Spectrochimie Infrarouge et Raman (LASIR)-UMR CNRS 8516, Epuipe Physico-chimie de l'Environnement. Une partie des travaux a été menée à l'Université Libanaise, Faculté de santé publique section III, au sein du Laboratoire des Sciences de l'Eau et de l'Environnement (L.S.E.E), Tripoli-Liban.

J'ai le plaisir de m'adresser tout d'abord mes sincères remerciements au Président de la Compagnie « Wildcat Oilfield Services » Dr. Abed Fattah Muriby pour la prise en charge, sans son aide je n'aurais pas réalisé cette thèse.

Je tiens à exprimer ma très grande reconnaissance à l'ensemble des membres de mon jury de thèse: Pr. Claude CASSELAS et Pr. Jalal HALWANI qui ont accepté sans hésitation de juger ce travail et d'en être les rapporteurs ainsi que Dr. Sopheak NET, Mme. Michèle TACKX et Dr. Ahmad TAMER qui ont accepté d'examiner et de faire partie de ce jury. Je tiens également à leur exprimer toute ma gratitude pour l'attention qu'ils ont porté à ce travail malgré leurs emploie de temps très chargés.

Je voudrais remercier en particulier mon directeur de thèse, Pr. Baghdad OUDDANE directeur de Master « Traitement des Eaux » pour m'avoir accueilli au sein du laboratoire et assurer la direction de cette thèse avec efficacité et rigueur en me laissant une grande liberté. Je le remercie pour son aide scientifique, ses conseils et sa grande disponibilité ainsi que les qualités humaines qui m'ont beaucoup appris.

J'adresse ma profonde gratitude Pr. Jalal HALWANI, directeur du L.S.E.E, pour son soutien scientifique, professionnel et je tiens également à lui exprimer ma gratitude.

Je suis également redevable à Dr. Sopheak Net, qui s'est toujours souciée de m'offrir, de tout point de vue, les meilleures conditions de travails possibles. Je la remercie en particulier pour sa grande disponibilité, ses grandes qualités scientifiques et la confiance qu'elle m'a accordée.

Je remercie également Dr. Ahmad TAMER, pour son accueil au sein du Port de Tripoli et sa patience pendant mes absences du travail durant ces trois années de thèse.

Mes remerciements vont également pour mon deuxième père Dr. Abed Fattah MURIBY Cette thèse n'aurait pu voir le jour sans son enthousiasme et sa confiance.

Au cours de cette thèse, j'ai par ailleurs été amené à effectuer plusieurs passages à L.S.E.E. Je remercie donc vivement Dr. Moemen BAROUDI et toutes les personnes pour leur accueil et leur assistance surtout Nadia, Hiba et Imane. Je remercie aussi très sincèrement mes collègues au Laboratoire Lasir à Shaza, Suzanah, Gabriel, Abdel, Wartel, Ludovic, David, Christine, Justine, Josselin, Anastazia, Pratima, Maya, Romain, Stevert, Siewert, Thomas, Pierre-Jean, et les autres doctorants ainsi que tous les stagiaires que j'ai eu la chance de les connaître et de passer avec eux de très bons moments.

Parmi ces remerciements, j'ai une pensée particulière pour mes collègues au Port Abdelrahman, Rouba, K., Omar, Rouba, M., Joudy, Mona, Ayman, et toute la famille du Port pour leur support et pour l'ambiance chaleureuse. Le travail à leurs côtés est un réel plaisir. Et un grand merci particulièrement à mes amies Rouba et yara pour leur aide et leur soutien apprécieux.

Je remercie mes amis et mes cousins Sara, Ranime, Farah, Wahib, Yahya, Mohamad, Abdallah, Hani, Alaa, Fadi, Taghrid et surtout à M. Ghassan MERHABY et également à mes amies Sali, Rayan, Khaled et Imad; membres de l'organisation « New Youth Generation Organization, NYGO ».

Un merci tout particulier à mes amies de longue date, fidèles et soucieuses qui m'ont beaucoup supporté, Layal, Mayssam, Dima, Abir, Doha, Angi, Fatat, Samah, Rasha, Nathalie, Sahar, Dalia, Hiba et surtout a Iman qui nous a laissé Tôt.

Je voudrais associer à ces remerciements à toute ma grande famille mes tantes Dawla, Nahla, Nada, Nahida, Fida et mes oncles Fawaz et Louay et leurs familles pour leurs encouragements et leurs soutien durant ces trois années.

Et Enfin, **Un GRAND MERCI** à mes parents, Ahmad Mezhar, Rajaa, ma grand sœur Zeina et sa petite fille adorable Sophie, mes frères Hussein, Mohamad et mon beau-frère Taha pour leur soutien et leur encouragement pendant toutes les longues années d'études et de thèse.

Merci

A vous tous …

RÉSUMÉ

La Zone Côtière Libanaise (ZCL) s'étend sur plus de 220 km le long de la mer Méditerranée orientale, est un cas typique de la plupart des zones côtières des pays en voie de développement où la combinaison d'un large éventail d'activités humaines contribue à la pollution de l'eau et à la dégradation de l'environnement. Cette pollution est due aux rejets industriels et domestiques, directs et indirects, d'un grand nombre de contaminants dans le milieu marin. En raison de son importance écologique, l'évaluation de la qualité des sédiments côtiers constitue un domaine de recherche important afin de statuer sur le niveau de la contamination des eaux. Dans ce travail, nous avons mis l'accent sur certains contaminants prioritaires tels que les Polluants Organiques Persistants (POP) et les élèments traces métalliques qui sont connus pour leurs toxicités, leurs bioaccumulations et les effets cancérigènes et mutagènes. En raison d'un manque d'informations sur ces polluants dans le bassin méditerranée orientale en général et sur la zone côtière libanaise en particulier, nous avons focalisé l'étude sur les sédiments dans les sites côtiers les plus sensibles comme les bassins semi-fermés tels que les ports et les baies qui sont des écosystèmes très vulnérables où une grande quantité de polluants s'accumulent dans les sédiments où la remise en suspension et l'oxydation des sédiments anoxiques se produisent fréquemment. L'évaluation de la qualité des sédiments portuaires est indispensable pour connaître le devenir en cas d'aménagement. Une attention particulière a été portée sur le site du port de Tripoli, qui est considéré comme le deuxième port du Liban et en raison de son emplacement à proximité d'une réserve naturelle classée, les îles palmiers. En général, le niveau de pollution de la ZCL varie entre moyen et élevé selon le site. Le Port de Beyrouth présente les plus forts niveaux de pollution organique et inorganique due à la contribution significative des activitiés anthropiques reliées directement ou indirectement au port, comme les activités industriels à l'intérieur du port ou aux alentours, en plus, de son emplacement dans la capital Beyrouth, ville la plus peuplée et urbanisée du Liban. Le Port de Tripoli est affecté significativement par les activités de pêches, de maintenance des navires et les rejets des eaux usées non traitées. Une proposition de plan d'urgence a été préparée pour l'aide à la décision des autorités du Port pour apporter des réponses aux incidents possibles comme les incendies ou le déversement pétrolier accidentel. Ce plan d'urgence peut être considéré comme une première étape de la gestion des zones côtières afin d'assurer un développement durable.

Mots-Clés: Liban; Métaux lourds; Mer Méditerranée Oriental; Polluants organiques persistants (POPs); Port de Tripoli; Plan d'urgence; Sédiments portuaires; Zone Costal Libanaise (ZCL).

ABSTRACT

Lebanon coastal zone (LCZ) which extends over 220 km along the Eastern Mediterranean Sea is a typical case of most coastal areas of the developing countries in the Mediterranean region, where the combination of a wide range of anthropogenic activities are contributing to water pollution and environmental degradation, by the direct and indirect release of a large number of pollutants into the sea via atmospheric and river inputs. Amongst the numerous environmental concerns we are facing, the marine environment is one of the top priorities that must be addressed. Due to its ecological importance, the evaluation of coastal sediment quality constitutes an important area of research to give a clear picture of water pollution status. Much attention was paid of some priority pollutants such as persistent organic pollutant (POPs) and heavy metals as known to be toxic, persistent and bio-accumulative, carcinogenic and mutagenic. There is an urgent need to survey the levels of these pollutants in sediments due to the great lack of information in the eastern part of the Mediterranean Sea in general and particularly in Lebanese coastal zone which render our study very important and useful regionally and locally by local authority and policy makers during coastal zone management. The semi-enclosed basins such as ports and bays are very vulnerable ecosystem where build-up greatly amount of these pollutants in sediments. This why we focus on our studies of the assessment of ports sediment quality of some possible hotspots where the re-suspension and oxidation of anoxic sediment occur frequently. A special attention was taken to Tripoli harbour which is the second Port of Lebanon due to its location near some reserved island. The pollution levels of LCZ by these pollutants are assigned as moderate to high. Highest organic and inorganic contamination was found at Port of Beirut which is significantly affected by the anthropogenic inputs inside the port such as effluent released from industrial activities and the surrounding area in addition to its location at Capital Beirut the most populated and urbanized city in Lebanon. Port of Tripoli is highly affected by the fishery and ship maintenance activitites and sewage outfall. An emergency proposal plan was prepared for Tripoli Harbour, this will assists harbour authority to response for all fire and oil spill accidents as a first step for a durable development inside this promising harbor.

Keywords: Eastern Mediterranean Sea; Emergency response plan; Heavy metals; Lebanese coastal zone; Lebanon; Persistent organic pollutants; Sediments ports; Tripoli harbor.

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Abbrevations List

ASE	Accelerated Solvent Extraction
ADR	Adriatic Sea
AEG	Agean Sea
ASTM	American Society for Testing and Materials
BaA	benz[a]anthracene
BaP	benzo[a]pyrene
BPEO	Best Practical Environmental Option
CBD	Convention for Biological Diversity
CDR	Council for Development and Reconstruction
CIEM	Conseil international pour l'exploration de la mer
CISIE	1ère Conférence internationale sur la sécurité intérieure des établissements
CLRTAP	Convention on Long-Range Transboundary Air Pollution
DDT	DichloroDiphenylTrichloroethane
DCMCP	Département de Chimie Minérale et Chimie Physique
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
EEA	European Environment Agency
EF	Enrichment Factor
ERT	Emergency Response Team
EF	Enrichment Factor
FSMP	Fire Safety Management Plan
GC	Gas Chromatograph
GPS	Global Positioning System
H	Henry's Law constants
HAP	Hydrocarbures Aromatiques Polycycliques
HCB	HexaChloroBenzene
HPLC	High-performance Liquid Chromatography
HSED	Health, Safety and Environment Department
HMW	High Molecular Weight
IBC	Incident Briefing Checklist
ICES	International Council for the Exploration of the Sea
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
I_{geo}	Geoaccumulation Index
ICZM	Integrated Coastal Zone Management
IEA	Integrated Environmental Assessment
IMO	International Maritime Organization
IMDG	international Maritime Dangerous Goods Code'
INERIS	Institut National de l'EnviRonnement Industriel et des RisqueS
ISO	International Organization for Standardization
K_{AW}	Air-water partitioning coefficient
K_{DOC}	Dissolved organic carbon partition coefficient
K_{OA}	Octanol-air partition coefficient
K_{OW}	Octanol-water partition coefficient
K_{OC}	particule organic carbon partition coefficient
Kp	Aerosols-vapour partition coefficient
LCZ	Lebanese Coastal Zone
L.S.E.E	Laboratoire des Sciences de l'Eau et de l'Environnement
LOQ	Limits of Quantification
MARPOL	International Convention for the Prevention of Pollution from Ships

MAP	Mediterranean Action Plan
MS	Mediterranean Sea
MED POL	the marine pollution assessment and control component of MAP
Me-PAHs	Methyl-Polycyclic Hydrocarbons
MMW	Medium Molecular Weight
MSPD	Matrix Solid-Phase Dispersion
MSDS	Material Safety Data Sheet
NCP	National Contingency Plan for Marine Pollution from Shipping and Offshore
NWE	Northwesten Mediterranean Sea
OCs	Organochlorine Compounds
OCN	OctaChloroNaphtalene
OCP	Pesticides OrganoChlorés
OEPT	Office d’Exploitation du Port de Tripoli
OPRC	Oil Pollution Preparedness, Response and Co-operation 1990 Convention
OSAC	Oil Spill Assessment Checklist
OSSC	Oil Spill Sampling Checklist
PAM	Plan d'Action pour la Méditerranée
PBTs	Persistent Bioaccumulative et toxic
PCBs	PolyChloroBiphényles
PCB-DL	PCB dioxine-like
PCDFs	Polychlorinated dibenzofurans
PCDDs	Polychlorinated dibenzo-p-dioxins
PLC	Personal Log Checklist
PLE	Pressurized Liquide Extraction
POP	Polluants Organiques Persistants
QA/QC	Quality Assurance and Quality control
RAC	Risk assessment Code
RT	Retention Time
SAE	Sediment Abou Ali Estuary
SCB	Sediment Chekka Bay
SE	Soxhlet Extraction
SLE	South Levantine Sea
SFE	Supercritical Fluid Extraction
SJB	Sediment Jouniyeh Bay
SLE	South Levanthine Sea
SQGq	Sediment quality guideline quotient
SQGs	Sediment quality guidelines
SOER	European environment - state and outlook
SPB	Sediment Port Beirut
SPJ	Sediment Port Jiyeh Power Plant
SPT	Sediment Port de Tripoli
SWE	Supercritical Water Extraction
TCN	TetraChloroNaphtalene
TYP	Tyrrhenian Sea
UAE	Ultrasonic-assisted Extraction
UNCLOS UN	Convention on the Law of the Sea
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environnent Programme
URGPGE	Unité de Recherche en Génie des Procédés et Génie de l'Environnement
US EPA	Agence de la protection de l’environnement aux Etats-Unis
V_D	Deposition velocity
V_p	Settling velocity
ZCL	Zone Côtière Libanaise

INTRODUCTION GÉNÉRALE

Le développement durable est une nécessité pour les générations futures, mais ce n'est pas facile à atteindre sur les échelles locales, régionales et mondiales. Ceci nécessite de garder l'équilibre entre ses trois composantes essentielles: les aspects économiques, sociaux et environnementaux. En effet, après la révolution industrielle, l'homme a introduit des dizaines de milliers de produits chimiques dans l'environnement, résultant des activités anthropiques multidisciplinaires y compris l'industrie, l'agriculture, le tourisme, le transport, la navigation et le commerce international. Compte tenu de l'augmentation du taux de développement économique, de l'urbanisation et de la croissance de la population, l'être humain a modifié significativement l'ecosystème, ce qui a conduit à des changements environnementaux et l'apparition des nouvelles maladies. Parmi ces produits chimiques présents dans l'environnement, les polluants organiques et inorganiques persistants trouvés à l'état de traces posent des problèmes importants et agissent comme une force évolutive sur l'écosystème. Les polluants organiques persistants (POPs) et inorganiques (métaux lourds) sont connus pour être toxiques, persistants, bioaccumulables et se transportent à des longues distance dans l'atmosphère et le milieu marin. Due à leurs propriétés physico-chimiques, qui déterminent leurs modes de transport, ces polluants se trouvent dans les différentes matrices environnementales entraînant des effets néfastes sur le milieu naturel et la santé humaine. Les éléments traces métalliques présentent un intérêt particulier, ils sont considérés comme toxiques puisqu'ils ne s'éliminent jamais de l'environnement par autoépuration. Au cours des quatre dernières décennies un effort important a été réalisé à l'échelle locale, régionale et mondiale pour étudier les sources d'émission, le comportement, les modes de transport, le devenir et les effets nocifs potentiels sur les écosystèmes et l'humain.

Malgré l'intervention de la communauté internationale par plusieurs initiatives telles que la Convention de Stockholm pour réguler, éliminer et arrêter la production de certains polluants (e.g. les pesticides organochlorés, OCP) et produits industriels (e.g. les polychlorobiphényles, PCBs) qui sont à l'origine des POPs dans l'environnement, ils sont toujours présents et même utilisés dans certains pays Méditerranéens à nos jours malgré l'interdiction. Ces polluants et notamment les métaux lourds sont significativement libérés dans le milieu marin par les activités anthropiques terrestres y compris les sources ponctuelles telles que les effluents industrielles, municipales et domestiques, rejets des navires, les apports fluviaux ainsi que les sources diffuses telles que le ruissellement, l'érosion et les dépôts atmosphériques. Les PCB ont été largement utilisés dans de nombreuses applications industrielles, ils sont classifiés parmi les déchets spéciaux. Ils ont été découverts pour la première fois en 1966 en tant que polluants de l'environnement, et ont été détectées dans l'eau, les sédiments, les oiseaux et les tissus des poissons. La présence des PCB est due à leur résistance à la dégradation, ce qui leurs permet de persister dans l'environnement pour des longues périodes et devenir très répandus dans l'atmosphère et le milieu marin. Le conseil international pour l'exploration de la mer (CIEM) a sélectionné sept congénères individuels (PCB 28, 52, 101, 118, 153, 138 et 180) les plus abondants dans les matrices environnementales. Récemment, une grande attention a été accordée au PCB dioxine-like (PCB-DL) du fait de sa toxicité élévée. Plusieurs études ont mis en évidence la formation de nouveau PCBs que de nombreux composés fabriqués industriellement sont émis par combustion reflétant. Autres polluants considérés comme sous-produits indésirables de la combustion et possèdent des caractéristiques similaires des PBTs (Persistent, Bioaccumulative et Toxic) tels que les hydrocarbures aromatiques polycycliques (HAP), ils sont classés par différents organisations comme des POPs, 16 HAPs ont été listés en tant que polluants prioritaires par l'agence de protection de l'environnement aux États-Unis (US EPA) en raison de leurs propriétés cancérigènes et mutagènes possibles ou probables. Egalement, Ils ont été détectés dans le sol, l'air et les sédiments ainsi que dans divers produits de consommations. Malgré l'origine naturelle, les apports anthropiques contribuent à la libération d'une grande quantité de HAPs, PCBs et métaux lourds dans l'environnement dus aux activités industrielles multiples et au transport maritime. Actuellement, ces sujets constituent un défi pour les scientifiques afin d'identifier les sources d'émission, de déterminer les propriétés physico-chimiques qui contrôlent leurs comportements, leurs modes de transport et leurs devenirs dans l'environnement ainsi que leurs effets toxicologiques négatifs.

La Mer Méditerranée est un bassin sensible due à l'augmentation de la pression exercée sur les zones côtières des pays développés et industrielles, ainsi que ses caractéristiques océanographiques le rend plus vulnérable à l'accumulation des polluants (mer fermée). Après avoir confirmé que ce bassin agit comme un puits et une source des contaminants persistants, un grand effort a été entrepris à l'échelle régionale comme l'établissement de la convention de Barcelone qui vise à protéger la mer Méditerranée et ses ressources contre la pollution. Un plan d'action pour la Méditerranée (PAM) et un programme de coordination (MED POL) ont été établis pour la recherche, le suivi, l'échange d'informations et l'évaluation des niveaux de pollution afin de prendre les mesures de protection nécessaires. Ce programme a été lancé en 1975, afin d'assister les capacités techniques des institutions méditerranéennes dans les pays en voie de développement et de fournir une base de données sur le niveau de pollution et particulièrement l'identification des sources. Malgré tous ces efforts, on trouve encore un manque important dans les données concernant plusieurs polluants et zones géographiques, particulièrement ceux qui sont localisées dans le sud et l'est de la Mer Méditerranéen, à l'exception de la côte égyptienne. Il est donc urgent d'étudier ces nouvelles régions dans ce bassin.

Le littoral Libanais qui s'étend le long de la rive orientale du bassin Méditerranée est exposé à un certain nombre d'activités anthropiques chroniques (e.g. la croissance démographique, l'urbanisation, les rejets des eaux usées et les effluents industriels non traitées) conduisant à la libération d'une quantité importante des polluants y compris les POPs et les métaux lourds dans la mer Méditerranée. Cette situation a été aggravée par les conflits du moyen orient en particulier la guerre avec Israèl en Juillet 2006, qui a entraîné le déversement de milliers de tonnes de pétrole dans la mer Méditerranée et récemment par le nombre croissant des réfugiés syriens. Le Liban est en période de reconstruction et transformation urbaine importante qui se manifeste par un développement commercial, résidentiel et industriel croissant. Plusieurs industries sont situées le long du littoral libanais, y compris deux ports commerciaux, plus de 15 ports de pêche, des dizaines de pipelines pour l'importation du pétrole, trois centrales de production de l'électricité et une série de diverses industries. En plus, plusieurs rivières se déversent dans la mer Méditerranée avec un apport important de pollution des bassins versants. D'un point de vue dynamique, les bassins semi-fermés tels que les ports et les estuaires où on trouve une pollution chronique due aux transports maritimes intensifs et à diverse activités industrielles. Cette situation exigent une étude approfondie des différentes sources d'émission notamment en raison du risque lié à la remise en suspension et l'oxydation des sédiments anoxique, qui a été identifié comme le processus clé de réintroduction des polluants dans la colonne d'eau, puis leurs absorption par les organismes aquatiques. Due à son importance écologique et la présence à des concentrations élevées des polluants dans les sédiments, ce compartiment constitue un domaine de recherche et un outil important pour donner une image claire sur le niveau de la pollution du milieu marin. Bien que le Liban a signé la Convention de Barcelone, que quelques études ont été conduites pour évaluer la pollution marine par les métaux lourds sans étudier la pollution organique des sédiments côtiers. L'objectif général de cette thèse est de déterminer le niveau de contamination en certains polluants organiques (HAPs, Me-HAP et PCBs) et inorganiques (métaux lourds) dans les sédiments de six stations distribuées le long du littoral libanais et d'évaluer le risque ecotoxicologique sur les organismes aquatiques afin d'avoir une image claire sur le niveau de pollution. Une attention particulière a été pris pour la zone portuaire particulièrement le port de Tripoli en raison de son emplacement à 5,5 Km d'une île protégée (e.g. île des palms).

Ce travail a été réalisé au Laboratoire de Spectroscopie infrarouge et Raman (LASIR) UMR CNRS 8516 de l'Université Lille 1 en France. Une partie de ce travail concernant les campagnes d'échantillonnages et la préparation des échantillons a été effectué dans le laboratoire des sciences de l'eau et de l'environnement à la Faculté de Santé Publique et au Port de Tripoli à Tripoli - Liban. Les travaux de recherche dans le cadre de cette thèse sont présentés en quatre chapitres.

Dans le chapitre 1 nous présentons des généralités sur les polluants organiques persistants sous forme d'une review, afin de fournir des informations sur les POPs; y compris les définitions, les différentes sources d'émissions, les classifications, les initiatives globales et régionales, les comportements, les modes de transport et le devenir dans l'environnement. Un focus est mis sur la distribution de ces polluants dans les sédiments des pays Méditerranéens afin d'identifier les zones à risques et leurs sources d'émissions essentiels.

Le chapitre 2 décrit la stratégie d'échantillonnage et les différents sites d'études et les méthodes d'analyses utilisées pour la détermination des HAPs, PCBs et métaux lourds dans les sédiments.

Dans le chapitre 3 nous présentons les résultats sous formes d'articles scientifiques publiés ou bien soumis dans différents journaux Internationaux. Le premier article est consacré à «La pollution organique dans les sédiments superficiels du port de Tripoli, au Liban» publié dans *Marine Pollution Bulletin*. Le second article soumis est une «évaluation des polluants organiques persistants dans les sédiments superficiels le long du littoral libanais». Le troisième article préparé pour une soumission est «Evaluation de la contamination inorganique dans les sédiments superficiels le long du littoral libanais».

Le chapitre 4 est consacré à la proposition d'un plan d'urgence pour répondre aux possibles accidents dus à des incendies ou des déversements d'huiles dans le milieu marin pour le port de Tripoli (OEPT). Ce travail est présenté sous la forme d'un article préparé pour une soumission intitulé «Plan d'urgence du port de Tripoli pour un Développement Durable (Liban)». Et enfin, nous terminons par une conclusion générale avec les perspectives de ce travail.

GENERAL INTRODUCTION

Go east go west the pollution is everywhere…!?

The sustainable development is a necessity for the future generations but is not an easy work to achieve it whether in local, regional and global scale. This require to keep balance between its three essential components: economic, social and environmental aspects. Indeed, after the industrial revolution humans have introduced more than ten thousands of chemicals in the environment as results of multiple anthropogenic activities including industries, agriculture, touristic, transport, shipping and international trade etc.. The increasing rate of economic development, urbanization and population growth the humans have significantly modified the ecosystem which leading to environmental changes then the appearance of new diseases. Among these chemicals, the persistent organic and inorganic pollutants found at trace levels in the environment can produce a significant threat and act as an evolutionary force for ecosystems. The persistent organic and inorganic pollutants (POPs and Heavy metals) are known to be toxic, persistent, bio-accumulative (PBTs), and prone a long-range atmospheric transport. They are transported by numerous processes depending on their use and physic-chemical properties to reach different environmental media and then can result in adverse environmental and humans effects, close and far, from their emission sources. The toxicity of trace metals take more concern, they are not removed from water and sediments by self-purification as the some organic compounds. Therefore, believe the increasing efforts at local, regional and global scale on their emission sources, behavior, transport, fate and potential harmful effects to ecosystems and human health during the last four decades. Although that the international community occur by different initiatives such as Stockholm convention to regulate and eliminate the use and production of some pesticides (e.g. organochlorine pesticides, OCPs) and some industrial products (e.g. Polychlorinated biphenyls, PCBs) but are still present in the environment and in used by some Mediterranean countries until today. These pollutants including heavy metals are also significantly released into marine environment from anthropogenic activities through land based sources including point sources such as industrial, untreated municipal and domestic waste water effluents, ships discharges, river inputs as well as diffuse sources such as surface runoff, erosion and atmospheric deposition.

PCBs were used extensively in many industrial applications and there are considered as an important class of special wastes. They were discovered for the first time as environmental pollutants in 1966, and were found throughout the world in water, sediments, bird and fish tissue and due to their resistant to degradation, which allows them to persist in the environment for a long time and become widespread via atmospheric and water transport mechanisms. International Council for the Exploration of the Sea (ICES) has selected seven individual congeners (PCBs 28, 52, 101, 118, 153, 138 and 180) as the most abundant in environmental samples. Recently, a great attention was rewarded to dioxin-like PCBs (DL-PCBs) because of their high toxicity. Recent studies have been highlighted that many industries produced compounds are also emitted during the combustion processes, which reflect a combination of new PCBs compounds. However, little are known about PCBs pollution but still a major concern. Other pollutant produced as undesirable by-product of pyrogenic process with similar characteristics of PBTs such as polyaromatic hydrocarbons (PAHs). These compounds were classified by different agencies as POPs and 16 PAHs were listed as priority pollutants by the United States Environmental Protection Agency (U.S. EPA) due to their possible or probable human carcinogenic and mutagenic properties. They have been detected in soil, air, and sediments as well as on various consumable products. Although their formed by natural processes but the anthropogenic inputs in particular that due to industrial and shipping activities contribute to a greatest amount of PAHs released into the environment as well as for PCBs and heavy metals. The multiplicity of their emission sources and transport mechanisms whether via atmospheric, rivers and oceans inputs and after that their health effects were known make them an interested topic of research. At the present time, it is a challenge for scientists to identify their emission sources, to determine their physic-chemical properties, which dedicate their behavior, transport and fate in the environment and their toxicological adverse effects.

Mediterranean Sea is a sensitive area due to the increase pressure exerted on coastal areas from both industrial and developed surrounded countries and its oceanographic characteristics (closed sea) which turn it vulnerable to the accumulation of many pollutants. The marine ecosystem can act as sink or source of these persistent contaminants to the environment, a great effort were taken on regional scale by the application of Barcelona conventions which aim to protect Mediterranean Sea and its resources versus pollution. A Mediterranean Action Plan (MAP) and Coordinated program (MED POL) were established for research, monitoring and information exchange; for assessment of the pollution state and the protection measures. This program was first initiated in 1975 and aim to assist the institution technical capabilities of Mediterranean from less developed and provide a database on marine pollution by collecting information on sources, concentrations levels and pollutants effects in the Mediterranean region. Despite all these efforts, there is still today a significant breaks in reliable data due to the information absence for many pollutants and non covered geographical areas in particular that located in the southern and eastern parts of the Mediterranean Sea exception of the Egyptian coast. Therefore, there is an urgent need to investigate and survey new regions in this part of the Mediterranean basin.

Lebanese costal area along the Eastern shoreline of Mediterranean Sea is exposed to a number of chronic anthropogenic inputs (e.g. growth population, urbanization, the release of untreated sewage and industrial effluent) that can contribute to the introduction of great amount of POPs and heavy metals into the Mediterranean Sea. This situation was further exacerbated by the Middle East conflict particularly the last Israeli-Arab war in July 2006, have drastically altered the east coastal Mediterranean sea by spilling of thousands tons of oil in the sea and recently by the increasing numbers of Syrian refugees. Lebanon is undergoing an exciting period of urban transformation, which has manifested in vast commercial, residential, and industrial property development. Several industrial plants are located along the coastal zone including two commercial ports, over 15 fishing harbors, dozens of sea pipelines for petroleum imports, three fuel power plants and series of various industries and factories in addition, to many river inputs into the Mediterranean sea. From a dynamic point of view, in semi-enclosed basins such as Ports and estuaries where occurred chronic pollution from shipping and other industrial activities requires more detailed fingerprinting of different contaminant sources particularly due to the risk related of the re-suspension and oxidation of anoxic sediment, which identified as key process capable of reintroducing these pollutants to the water column then to aquatic organisms and the atmosphere.

Due to its ecological importance, the evaluation of coastal sediment quality constitutes an important research area and a tool to give a clear picture of water pollution specially that the concentration of these pollutants is much higher than in water column. Although that Lebanon has signed the Barcelona convention but a few studies were conduct to assess the heavy metal pollution without studying the organic pollution in coastal sediments. The overall objective of this work is to investigate the level contamination of some organic and inorganic pollutants in sediments and assess their Ecotoxicological risk on aquatic organisms at six hotspots distributed along Lebanese coastal zone in order to draw a clear picture about the level of pollution by these pollutant and a special attention were taken for Ports area and specially Tripoli Harbor due to its location at 5.5 Km away from some reserved islands (e.g. Palm Island). This work was performed as a PhD thesis at Lille 1 University. All analysis was carried out in the Laboratory of Spectrochimie Infrared and Raman (LASIR) -UMR CNRS at Lille 1 University in France and part of work concerning sampling campaigns and samples preparation was conducted in the Laboratory of water Science and Environment in the Faculty of public Health of Lebanon University and in Tripoli Port - Lebanon. This thesis is organized into four chapters.

Chapter 1: an overview on persistent organic pollutants is presented in form of review, in order to provide a comprehensive information on POPs; including definitions, different emission sources, classifications, global and regional initiatives, their behavior, transport, fate and their occurrence and distribution (PAHs and PCBs) in sediments for the Mediterranean Sea in order to identify the hotspot zones and their essential emissions sources.

Chapter 2: Description of sampling campaigns, studied sites and the analysis strategy adopted for the determination of PAHs, Me-PAHs, PCBs and trace metals concentrations in sediments.

Chapter 3: All results obtained are presented in the forms of published or submitted papers to different international journals. The first paper is about “Organic pollution in surficial sediments of Tripoli harbor, Lebanon” published in *Marine Pollution Bulletin*. The second submitted paper is an “Assessment of Persistent Organic Pollutants in surficial Sediments along Lebanese Coastal Zone”. The third paper prepared for Submission is an “Assessment of inorganic contamination in surficial Sediments along Lebanese Coastal Zone”.

Chapter 4: Proposal of a contingency plan to response for fires and oil spill accidents prepared for Tripoli Harbor (OEPT) presented in form of paper prepared for submission subtitled “Tripoli Harbor Contingency Plan for a Durable Development (Lebanon)”. And finally, a conclusion with prospects of thesis research work will be presented.

CHAPTER 1

LITERATURE REVIEW

Review

Overview of POPs in Mediterranean Basin: Transport, Fate, Occurrence, and Distribution

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Paper Prepared for Submission

00/00/2015

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Abstract

Humans have greatly modified the biosphere by the release a great amount of toxic chemicals into the environment. The persistent organic pollutants (POPs) are among the most toxic chemicals release mainly from human activities. Multiples anthropogenic activities contribute to this pollution directly and indirectly whether by primary or secondary sources. Their physico-chemical characteristics as a toxic, persistent, bioaccumulative dedicate their behavior, transport and fate in the environment. And because of their capacity to be transported at long range in the environment, the POPs can reach areas far from their emission sources and accumulate in abiotic and biotic environmental matrices. Higher concentrations of POPs were found close to urban source areas due to the importance of coarse particles and ambient temperature influence the equilibrium and mechanisms of air-sea exchange. Sediment is not considered as final reservoir but also a sink and source of these POPs. Due to different environmental or anthropogenic events these pollutants can be remobilized and desorb to join the re-cycling environmental processes and accumulate in phytoplankton and aquatic organisms up to food chain. Major efforts were paid 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. CLRTAP protocol and UNEP Stockholm 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. Although, the activities of MED POL program, we still observed a significant gaps in reliable data concerning many pollutants and geographical areas particularly that located in the southern and eastern parts of the Mediterranean. A study survey of the distribution of some PAHs and polychlorinated biphenyls (PCBs) concentrations were conducted in this review for Mediterranean region. As results numerous hotspots Mediterranean countries and several sub-hotspots were identified are mostly concentrated in NWE, TYR, ADR, AEG and SLE (Egyptian coast) Sea. High contamination levels were detected in sediment samples collected from bayous and harbors, lagoons and river mouths. Also a great lack in information also related to open sea and deep sediment make it to take a definitive conclusion about the situation of Mediterranean regards PAHs and PCBs pollution suggesting it is in critical situation and is not in very good health. Is recommended to create a regional cooperation network and monitoring programs for Mediterranean countries and adoption an integrated environmental assessment (IEA) approach that allows to increase the communication between decision-makers, research community, public and industries.

Keywords: POPs, Pollution, Mediterranean Sea and Hotspots.

Introduction

Anthropogenic driven forces leading to POPs release in the environment

Last six decades, the human driven impact on the environment has been increased exponentially. Anthropogenic driving force constituted by the irreversible modification and perturbation of ecosystem function and structure including atmosphere, water, sediments, and biota composition since thousands of organic chemicals at ultra-trace levels has been introduced to the environment (Daughton, 2005; Muir and Howard, 2006). This 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). Recently, many agencies develop new prioritization scheme for the untested POPs such as NORMAN Prioritization scheme for emerging substances developed by INERIS (L'Institut National de l'EnviRonnement Industriel et des RisqueS), France (Slobodnik, 2015) (http://www.norman-network.net/). These chemicals come from many different applications ranging from agricultural herbicides, insecticides, pharmaceuticals, detergents, flame retardants, insulating materials, di-electric fluids, combustion by-products and many other applications (Vallack et al., 1998; Muir and Howard 2006; Schwarzenbach et al., 2003). Then, they can be transported close and 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 several 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).

Definition 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) (Herrman, 1993; Birnbaum, 1994; 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). In this context, ‘substance’ means a single chemical species, or a number of chemical species which form a specific group having similar properties and being emitted together into the environment or forming a mixture marketed as a single product (Vallack et al., 1998).

Persistent Organic Pollutants or POPs are a subclass of PBTs that are prone to long-range atmospheric transport and deposition. 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, PAHs, etc.) (Dachs and Méjanelle, 2010; Jones and De Voogt, 1999). 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.

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)**
Organochlorine Pesticides			
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)
Industrial products			
Hexabromobophenyl [a,d]			
Polychlorinated biphenyls (PCBs) [a,b]	1930-1993	1326 kt	Breivik et al. (2007)
Unintentional by-products of combustion and industrial processes			
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).

Origin of different family of POPs

Historic Production and use

From 1950 to 1980, huge quantity of pesticides was used for the protection of crops and to prevent from health diseases in the world. Five organochlorine pesticides (DDT, chlordane, heptachlor, mirex and toxaphene) among eight has been produced on an industrial scale in China while the other three (aldrin, dieldrin and endrin) has been produced during pilot projects or in research. 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). Hexachlorobenzene (HCB) was used as a fungicide and it is generated as a by-product in many combustion and industrial processes. Its production was estimated at 30,000 t year $^{-1}$ in 1981 in Europe (ECETOC, 1988) and in the order of 1000 t year $^{-1}$ in the Mediterranean region by mid 1980s (UNEP, 2002). 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. The extensive use of pesticides lead to serious contamination in soil, air, water, sediment, food and cooking oil, especially to edible animal meat (Yang, 1989). And, trace levels of pesticides have been found in soil, crops, vegetables and in fruits declining steadily after the prohibition (Zhang and Yang, 1996; Shan et al., 1997). Therefore, series of rules and regulations intended to address the management, production and use of pesticides within the country was established by the government of China. Nowadays, DDT is still in use but it is limited as stock for Dicofol and to control vector of malaria disease. Chlordane and mirex have been banned as general use pesticides, but they are still produced for termite control due to limited alternatives. The production and development of toxaphene, heptachlor, aldrin, dieldrin and endin is forbidden (Yao and Zhang, 2001; Cheng, 2001). 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.

POPs emission sources

POPs sources can be divided between primary and secondary. Primary sources are those directly related to chemicals application (e.g. pesticides or accidentally released PCBs from old equipment, etc...). 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 (e.g. direct spills and rivers) (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. 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., Larsson, 1985; Harrad et al., 1994; Jeremiason et al., 1994), or due to primary emissions (e.g., Jaward et al., 2004; 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., 2004) without confirmation whether these are due to primary (e.g. volatilization from electrical equipment or building materials) or secondary sources (re-emissions from contaminated environmental hot spots) (Hsu et al., 2003; Uraki et al., 2004). Whereas, higher molecular PAHs due to their strong sorption to atmospheric particles were controlled primary by atmospheric emissions (e.g., 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 (Jones and De Voogt, 1999; Dachs et al., 2010).

Source identification

At the present time, there is a challenge for scientists to create an approache 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 PYR and FLA tend to accumulate in the gaseous phase, whereas PAHs heavier than BaA 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.

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*

POPs classification

POPs can be classified into two categories: 10 intentionally produced chemicals including organochlorine pesticides such as: DDT, aldrin, endrin, merix, dieldrin, heptachlor, toxaphene, and chlordane and industrial chemicals such as: PCBs and HCB and unintentionally produced by-product like dioxins, furans and polycyclic aromatic hydrocarbons (PAHs) (Jones and De Voogt, 1999; UNIDO, 2000; Fiedler, 2003; Zhang et al., 2005, 2009; El-Shahawi et al., 2010) (Fig. 1).

Intentionally POPs

These organic compounds were produced as wanted products by different chemical reactions that include chlorine. This link between organic molecules and chlorine atoms their exhibit high lipophibicity and, usually, high neurotoxicity characteristics and they are called organochlorine compounds (OCs). In addition, this category includes several compounds which can be divided into two types: industrial chemicals and organochlorine pesticides (Kelce et al., 1995; Harner et al., 2006). Examples of OCs are the chlorinated insecticides, such as dichlorodiphenyltrichloroethane (DDT), and polychlorinated biphenyls (PCBs). As following description of these examples intentionally POPs compounds:

Organochlorine pesticides

DDT is an organochlorine pesticides was widely used in crops to control diseases propagation by insects and its cumulative global usage was estimated in around 4500 kt for the period 1940 - 2007 (Table 1). In the 1970s, the use of DDT was banned in many developed countries, but it was produced until middle 1990s in Europe and is still in use for some purposes in some Mediterranean countries (UNEP, 2002).

Industrial chemicals

PCBs are a class of organic compounds with chemical structure formed with 2 - 10 chlorine atoms attached to the biphenyl molecule (Fig. 2). Theoretically, there are 209 different PCB congeners. PCBs were used extensively in many 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, lubricants in the treatment of wood, clothes, paper and asbestos, pigments and as dispersing agents in formulations of aluminum oxide (Korytáret al., 2002). Although their production ended in the late 1970s, the majority of the cumulative world production of PCBs are still in the environment due to their resistant to degradation, which 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. 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). 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). Recently, growing attention was focused to the so-called dioxin-like PCBs (DL-PCBs). PCBs substituted in only one 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).

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: dioxin and furan compounds and polycyclic aromatic hydrocarbons (PAHs) (Fig. 1). 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 grates 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 (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. 2 (A).

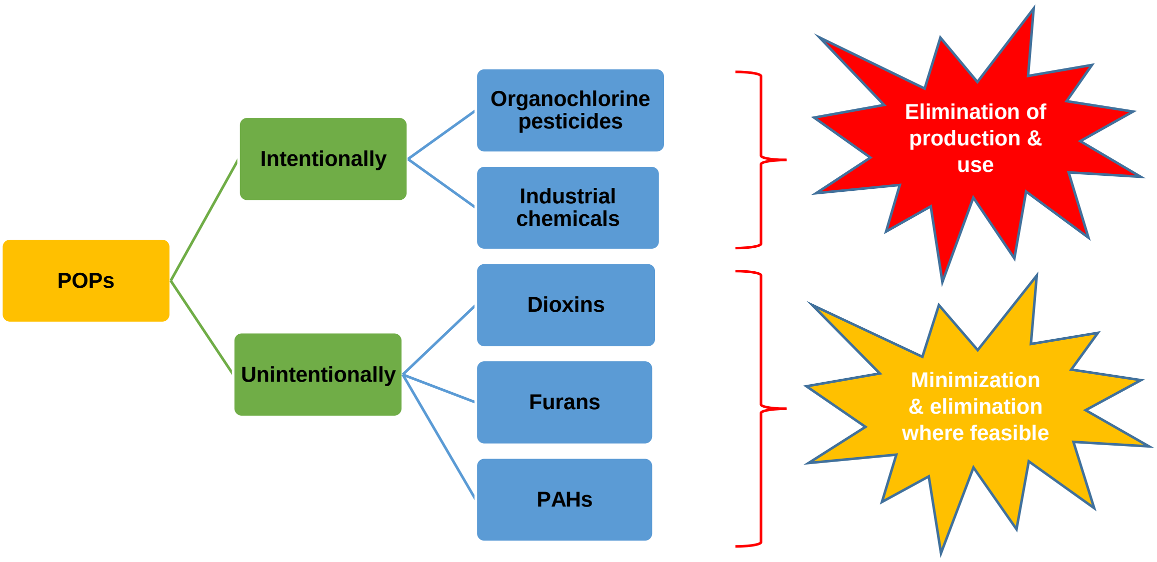


Fig. 1 : POPs classification

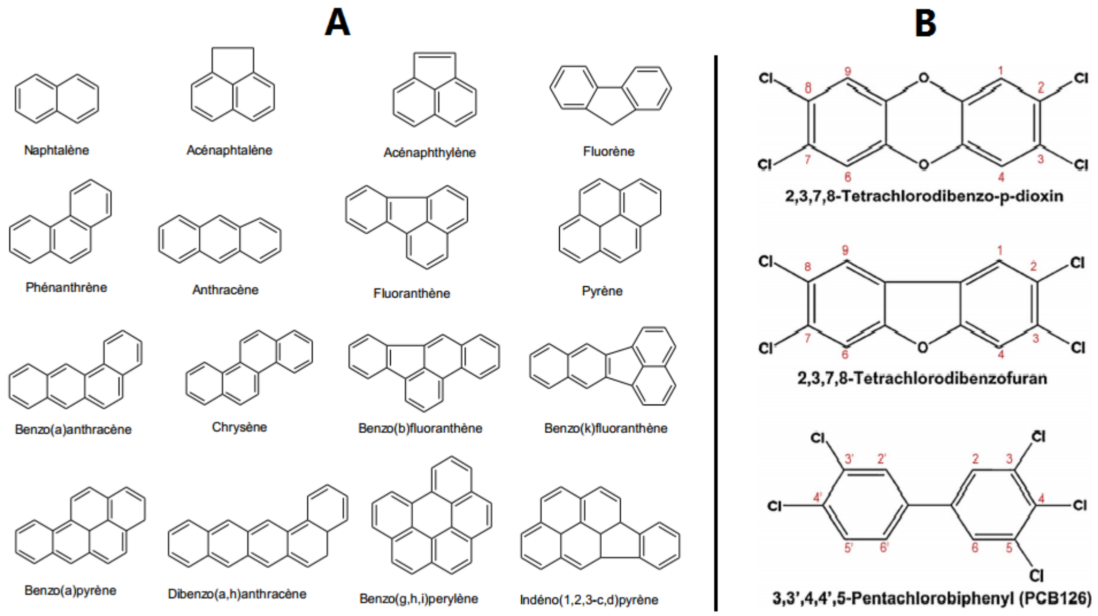


Fig. 2 **A**: Structure of 16 PAHs listed as priority compounds in the U.S. EPA and **B**: basic structures of polychlorinated biphenyls (PCBs), chlorinated dibenzofurans (furans) and Chlorinated dibenzo-p-dioxins.

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 km^3 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 (Fowler, 1986; 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). Many studies shows that the main driving forces in the Mediterranean Sea are related to the urbanization, tourism, industrial production, intensive agriculture, ports and shipping activities (EEA, 1999; Gómez-Gutiérrez et al., 2007; Dachs et al., 2010; Berrojalbiz et al., 2011). Recently, Gómez-Gutiérrez (2007) has reviewed in its assessment study of Mediterranean Sea that the cities and river inputs pose an increasing pressure onto the Mediterranean coastal areas (EEA, 1999; Anna Gómez-Gutiérrez et al., 2007; Berrojalbiz et al., 2011), which may cause a negative impact in coastal and marine ecosystem, and subsequent risk on natural resources (EEA, 1999). 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 (Jones and de Voogt, 1999; Loganathan and Kannan, 1994) 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 (De Voogt and Brinkman, 1989 ; 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).

Fig. 3: 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

Regional and global initiatives and conventions

POPs Global initiatives

There have been several milestones of international chemical management considering POPs such as the 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: 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).

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” 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 (the 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 is 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, Co-ordinated 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 concentrations and effects of pollutants in the Mediterranean region. Involves more than 100 Mediterranean research and monitoring institutions and it is coordinated unit Centre is located in Athens (Gabrielides, 1996).

However, despite all these international interventions started since 1972s, there is still 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. 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 GDPs and the application of environmental control and management measures (Anna 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; 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.

Behavior, Transport and fate of POPs

The physicochemical properties which were attributed to POPs dedicate their behavior, transport and fate in the environment (Wania et al., 1998; Jones and De Voogt, 1999; El-Shahawi et al., 2010). These are determined by the structure of the molecule and the nature of the environment (Fig. 2). 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 (Berg et al., 1998; Jones and De Voogt, 1999; Guzella et al., 2005; Grassi et al., 2010). This why, they possessing 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, DDT and OCPs can be classified as multi-hoppers (Wania, 2003, 2006) while PAHs act as single hoppers (Lohman et al., 2007), and HCHs as a swimmers. Due this multi-hop nature of POPs to relate their deposition rates to emission rates is a very complicated matter (Wania, 1997). 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. Generally, overall degradation rate is estimated by a half-life value were suggested two days, two months and six months in air, water and soil/sediment respectively (Vallack et al., 1998). It should be noted here that 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 their 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. The atmospheric deposition across air-sea interface exchange is considered 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 (diffusive vapor exchange, precipitation scavenging of vapors and particle-sorbed chemicals), 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).

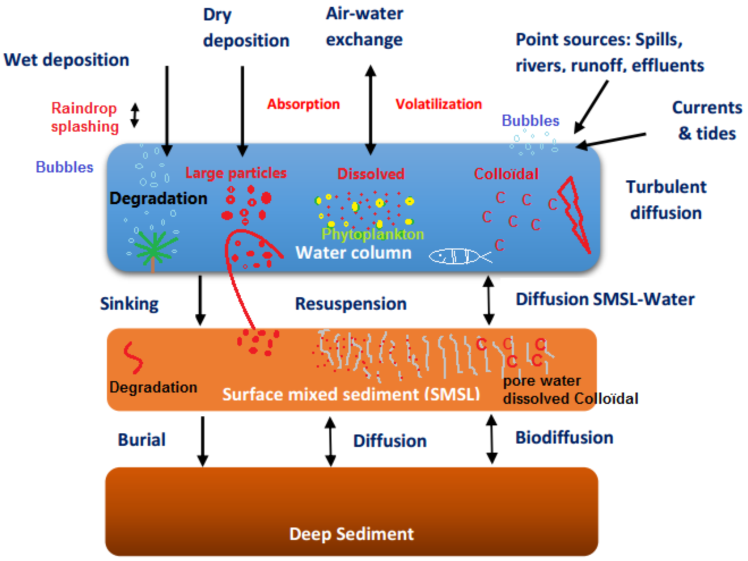


Fig. 4: Schematics of the processes driving the environmental fate of POPs in coastal waters (modified Dachs and Méjanelle, 2010).

Vapor-particle partitioning: in the atmosphere is mainly controlled by the absorption of these POPs in organic carbon which is the most abundant component in atmospheric fine aerosols and has a strong influence on the fate of POPs in the aquatic and terrestrial environment (Pankow, 1994a, b; Heintzenberg, 1989). In the CLRTAP POPs protocol is suggested that POPs exhibit a vapor pressure criterion of < 1000 Pa but may be preferable to use the octanol-air partition coefficient to give an excellent characterization of partitioning from air to aerosols (Vallack et al., 1998). For example, concentrations of atmospheric $\sum_{41}$ PCBs are ranged from 389 to 1410 pg/ m^3 in the gas phase and from 71 to 78 pg/m^3 in the aerosol phase in off-shore Barcelona (García-Flor et al., 2009) and in Banyuls-sur-Mer, France, PCB concentrations were found as 30.7–858 pg/m^3 in the gas phase and 12.8 - 41.2 pg/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 (Murphy et al., 1981; Strachan and Eisenreich, 1988; 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 m/s, with a geometric mean of 0.0046 m/s. Some studies has derived a V_D of 0.0037 m/s for particle-bound PAHs (McVeety and Hites, 1988) while for total PCB are 0.001-0.005 m/s (Eisenreich et al., 1981), 0.0016 m/s (Swackhamer et al., 1988) and 0.0038-0.0051 m/s (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 the molecules 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 organochlorinated compounds 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 at higher temperatures for air side, whereas the rate of absorption (N_{AW}) decreases at higher temperatures for water side. 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. Also, 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). 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).

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 (caused by Brownian motion and turbulence) causing small particles to aggregate, grow and settle (Wania et al., 1998). 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). Addition processes other to volatilization, can contribute to the transfer of POPs from the water to the atmosphere are bubbles created during the breaking of waves and as a result of extensive photosynthesis by marine algae and raindrop splashing especially during heavy rainstorms associated with strong winds (Green and Houk, 1979; 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).

Effect of Temperature and seasonal variation

All these deposition pathways of POPs are strictly depended from temperature and seasonal variation and subsequently in the global and regional distribution behavior and fate of POPs in the environment (Mackay and Wania, 1995) (Fig 4). In the case of vapor- particle portioning, POP concentrations on particles tend to be 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. Preliminary limited estimates and measurements suggest that snow may indeed 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 a whole range of meteorological and physical factors, such as the vertical distribution of particles and precipitation intensity. Koester and Hites (1992) have observed that the higher percentages of PCDD/Fs bound to particles at lower temperatures. The equilibrium partitioning between air and water, as expressed in Henry's Law constants (H), is highly temperature dependent for more information see Wania et al., (1998).

Based on these deposition and re-cycling routes different coefficient partitioning coefficients were predicted such as: octanol-air partition (K_{OA}), aerosols-vapour partition coefficient (K_p), octanol-water partition coefficient (K_{OW}), air-water partitioning (K_{AW}), particule organic carbon partition coefficient (K_{OC}) and dissolved organic carbon partition coefficient (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 octanol-water partition coefficient (K_{OW}) and thus have high affinity to organic matter to which they sorbed (Jurado et al. 2004) (Fig. 5). Water solubility, vapor pressure and biodegradability are low and decrease with an increasing degree of PAHs rings and chlorine substitutions while hydrophobicity and sorption tendency increase (Arslan-Alaton and Olmez-Hanci., 2013), because this hydrophobicity is determined by their structure as mentioned previously. The Variation of the water solubility (S_W), Octanol-water and Octanol-particulate carbon partition coefficients (Log K_{OW} and Log K_{OC}) for some POPs (PAHs and

PCBs) according to the numbers of (A) PAHs rings and (B) PCBs Chlorine atoms is show in Fig. 5. There is clear that POPs with same physicochemical properties have similar trends, pathways and fate in the environment.

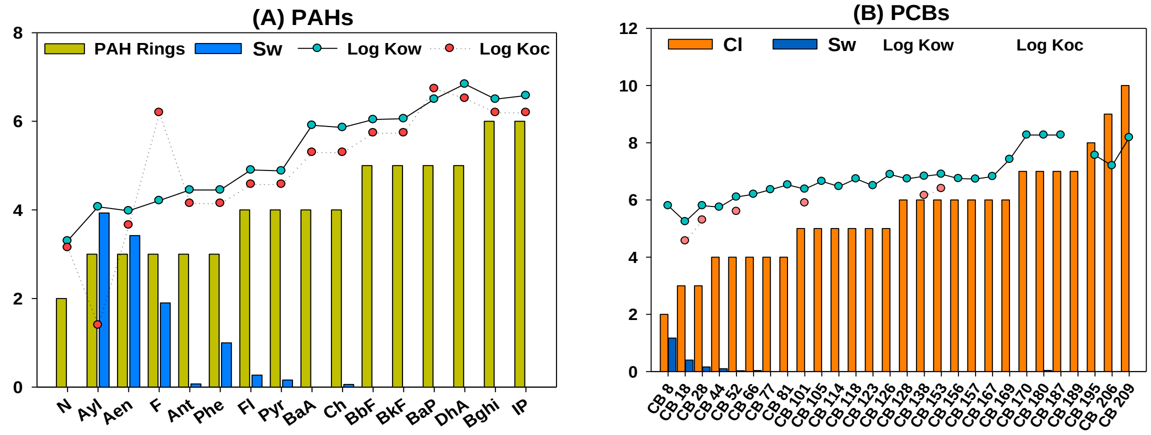


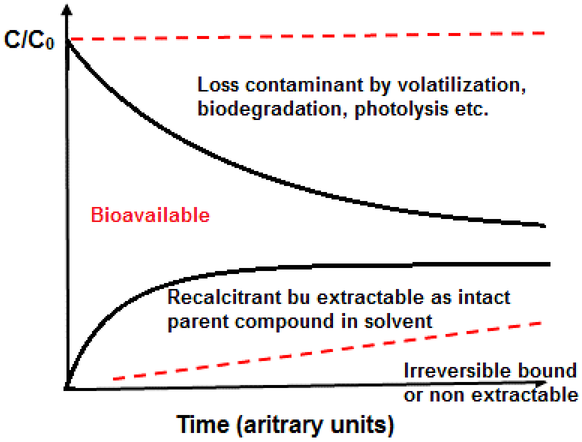
Fig. 5: The Variation of the water solutbility (S_W), Octanol-water and Octanol-particulate carbon partition coeffcient (Log K_{OW} and Log K_{OC}) partitioining coeificient for some POPs (PAHs and PCBs) according to numbers of (A) PAHs rings and (B) PCBs Chlorine atoms.

Grain size and organic matter content

These two characteristic play an important role in the sorption behavior of POPs on atmosphere and water column. Due to their low S_W and high partitioning coefficients like K_{OW} and K_{OC} (Fig. 5), POPs have high affinity for solid matrices (Ozcan et al., 2009; Zhao et al., 2010). Most studies has been reported that the 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 different PAHs molecular weight (Pistikopoulos et al., 1990; Aceves and Grimalt, 1993; Allen et al., 1996) and degradability (e.g. Pistikopoulos et al., 1990; Venkataraman and Friedlander, 1994). 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). Kaupp et al. (1994) found that 90% of PCDD/Fs were found on particles with aerodynamic diameters of <1.35 µm. 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. Is very clear, that the cycling of POPs in the environment is depended also to their absorption by organic carbon.

As a consequence of this persistence, low water solubility and high Log K_{OW}, POPs can accumulate relatively at 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. 4) (Thomann et al., 1992) whereas for higher trophic levels dietary uptake is by direct absorption (UN-ECE, 1994). Berrojalbiz et al., (2011) was observed a significant dependence for the most persistent Organochlorine Compound concentrations (C_p) (OCP; PCBs and HCB) in plankton with biomass in Mediterranean Sea (Berrojalbiz et al., 2011). This significance correlation between C_P and the biomass (PCBs; $R^2 = 0.58$, $p < 0.01$ and HCHs; $R^2 = 0.61$, $p < 0.01$) has been hypothesized to be driven by the named "biomass dilution effect" in plankton and biomass in Mediterranean Sea (Larsson et al., 2000). Numerous studies show that POPs such as PCBs, DDT and HCB bioconcentrate in phytoplankton (Dachs et al. 1999a, b; Berrojalbiz et al. 2009), bacteria (Wallberg & Andersson 2000), and bioaccumulate in higher trophic webs (Gobas et al. 1999; Restrepo et al. 2005; Arias et al., 2015). Their resistance to chemical and metabolic degradation led to increase their concentrations in fatty tissue, this phenomena namely biomagnification can lead to concentrations in top predators many orders of magnitude higher than in the environment (Vallack et al., 1998; Gobas et al. 1999; Dachs and Méjanelle, 2010).

The evidence of this atmospheric long-range transport of POPs, it is clearly that these pollutants have resistance to photolytic, biological and chemical degradation (Vallack et al., 1998). Indeed, the degradation and bio-availability processes of POPs are less studied and consist a very interested topic for researchers. Based on the strong bounds between POPs whether for PAHs and PCBs (carbon-carbon/carbon-chlorine bounds) with coal derived particles which was described before make them very stable toward hydrolysis and this greater resistant to biological and photolytic degradation is due to the significant number of phenolic rings and chlorine substitutions (functional group). So, they can persist in the environment for long time. This phenomenon is referred to bioavailabilities were the need to develop a new technologies to reduce their emissions from some station sources and for sediment and soil treatment in some hotspots areas (Chu et al., 2006). Previous studies show that 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). For the best of knowledge, an important process influence POPs concentrations in soils and sediments which decrease due to the "ageing" effects producing non-extractable residues (parent or breakdown product) over time, then 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.



C_0 = Concentration at time t =0; C= Concentration at t.

Fig. 6: Conceptual graph of the possible forms of POPs in soil and sediment (Jones et al., 1999).

Occurrence and distribution in Mediterranean basins

Mediterranean Sea is considered as a sensitive basin and a very interesting region for studies. Gabrielides (1996) has reported, based of 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 MS in the vicinity of coastal areas in particular these close to industries and population centers. Sediments can be an important sinks 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 Mediterranean Sea (MS) data regarding PAHs and PCBs concentrations (µg/kg d.w.) 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 Mediterranean Sea, only twelve countries have published research papers on POPs. The most studies with approximately 75 % 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 on POPs 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 %).

Fig. 7 shows the total mean concentrations of the $\sum_{10-26}$PAHs and $\sum_{7-41}$PCBs in the sediments for each studied 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).

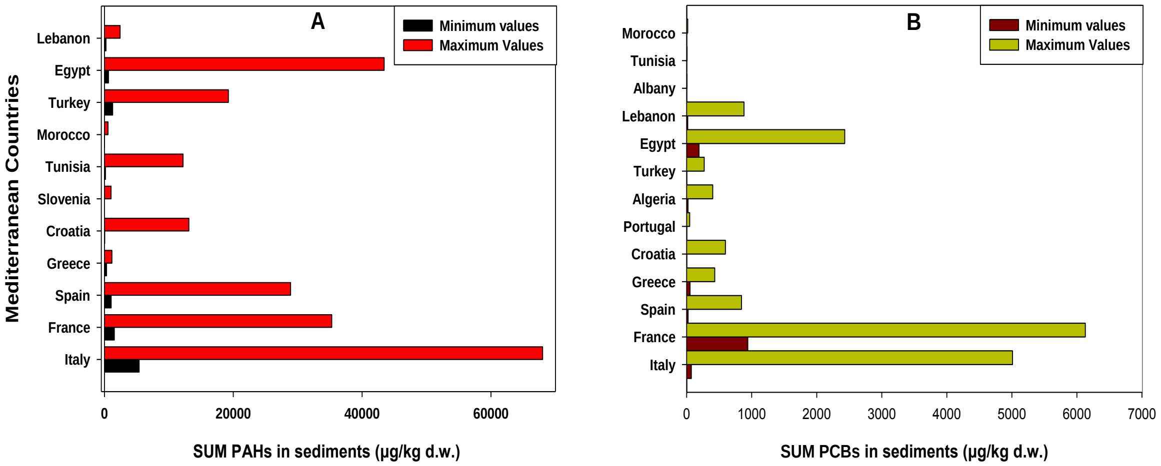


Fig. 7: The total mean concentrations of PAHs **(A)** and PCBs **(B)** in sediments for each Mediterranean country.

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 shown the contribution of each category in the total mean concentrations of the $\sum_{10\text{-}26}$PAHs and $\sum_{7\text{-}41}$PCBs in the sediments for each studied Mediterranean country.

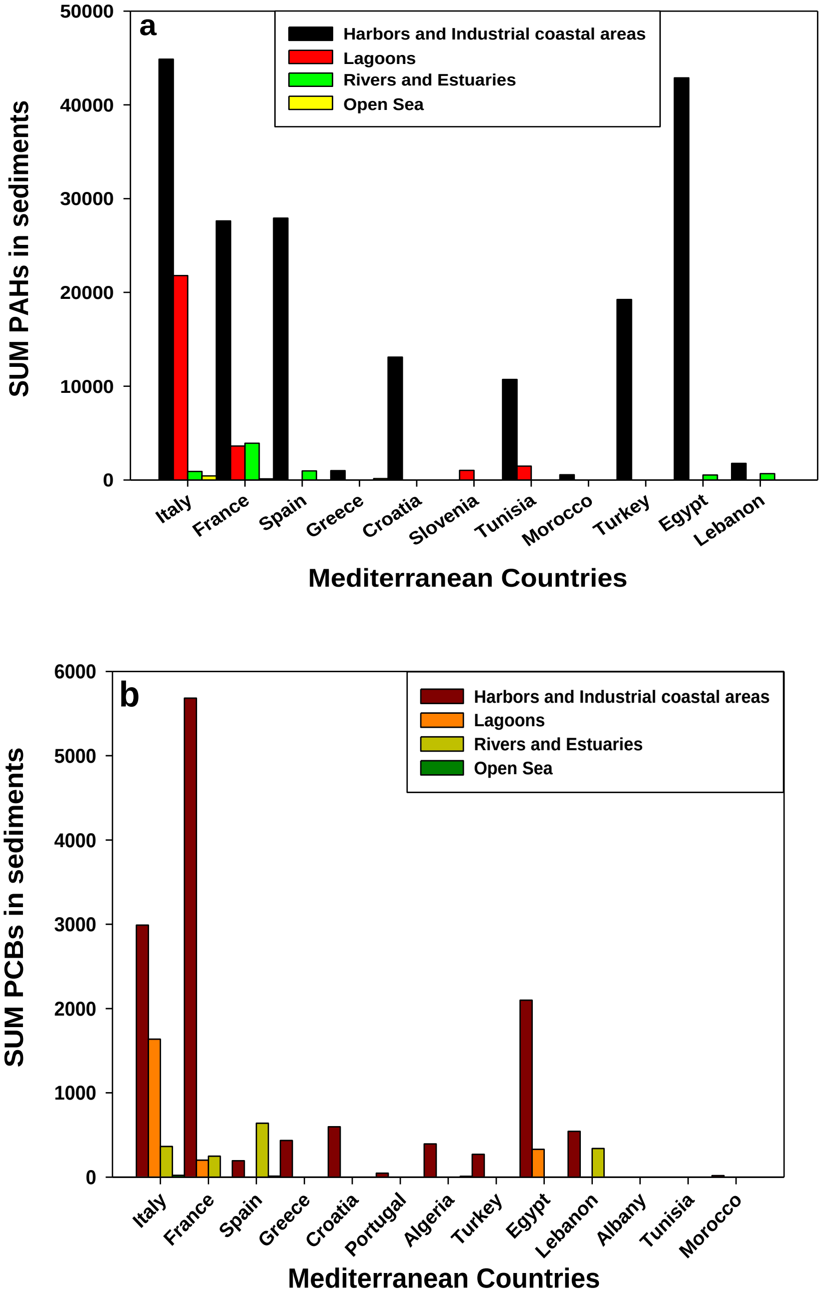


Fig. 8: Total mean concentrations of the ∑10-26PAHs (a) and ∑7-41PCBs (b) in sediments of each Mediterranean country for the four categories.

PAHs distribution in Mediterranean Basin

Harbors and industrial coastal areas are the most contaminated sites with PAHs in almost all studied sites of Mediterranean basins (Fig. 8a). Table 3 summarized the highest total concentrations of ∑PAHs in sediments collected from Mediterranean sites. In Italy, the highest PAHs concentrations were reported for Gulf of Taranto (262446 µg/kg d.w.) followed by Lazaret bay, France (48090 µg/kg d.w.) (Cardellicchio et al., 2007; Benlahcen et al., 1997) (Table 3). In fact, Gulf of Taranto was the most polluted site in Mediterranean Sea. Indeed, Gulf of Taranto 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 are demonstrated also by the concentrations found in Alexandria harbor in Egypt (13150 µg/kg d.w.), Naples harbor in Italy (31774 µg/kg d.w.), Ajaccio harbour in Corse-France (20440 µg/kg d.w.), Lazaret navy harbour in France (13010 µg/kg d.w.), Sfax-Kerkennah Coast in Tunisia (10720 µg/kg d.w.) and Barcelona harbor in Spain (10320 µg/kg d.w.) (Table 3). In Turkey, Tolun et al. (2001) have reported that ∑PAHs were 2500 - 25000 µg/kg d.w., while Telli-Karakoç et al., (2002) have found at 30000 - 167000 µg/kg d.w at Izmit Bay. 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 µg/kg d.w.). Above all, we can suggest that harbor sediments of MS were significantly polluted by the ∑PAHs.

Also, the results show that a significant PAHs contamination was found for lagoons in some Mediterranean countries. Highest ∑PAHs concentrations were found in Pialassa Baiona lagoon, in Italy in the range of 1000-135000 µg/kg d.w., (Vassura et al., 2005; Guerra, 2011). High concentrations were also detected in other Italian hotspot lagoons such as Venice Lagoon (65 - 48000 µg/kg d.w.) and Mar Piccolo in Taranto (380 - 12750 µg/kg 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 concentration was found near to the harbor area of the Italian Military Navy due to the influence of shipyard activities. Obviously, harbors have the significant pressure 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 scare hydrodynamism and low water exchange But we should to note that ∑PAHs concentrations were decreased with time in the range of (315 - 810 µg/kg d.w.), (20 - 502 µg/kg d.w.) and (15 - 389 µg/kg d.w.) such as reported by Frignani et al., (2003), Parolini et al., (2010) and Secco et al., (2005), respectively (Table 3). Similarly to that suggested for Pialassa Baiona lagoon this decrease of ∑PAHs concentrations may because that Venice lagoon was subjected to special laws to preserve and improve its environmental quality and/or may be due to environmental re-cycling processes. In France, the highest ∑PAHs concentrations was observed at Thau and Berre lagoons with ranges 59 - 7679 and 38 - 2323 µg/kg d.w. respectively. The concentration of ∑PAHs decreased in Berre lagoons to reach maximum concentration of 853 µg/kg d.w (Kanzari et al., 2003) (Table 3). However, the increase of highest ∑PAHs concentrations in Bizerte lagoon in Tunisia from 447.1 µg/kg d.w. in 2005 to 2500 µg/kg 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 around this lagoon.

The riverine inputs play an important role in the transition of PAHs to the MS in some countries. In France, highest ∑PAHs concentrations in the Rhone Delta (river mouth) were in the range of 1070 - 6330 µg/kg d.w., have been reported by Bouloubassi and Saliot (1993) while Lipiatou and Saliot (1991) have been found at 325 – 3182 µg/kg d.w. (Table 3). High ∑PAHs were also found in Griond estuary with the range of 185 - 4888 µg/kg 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 PAHs concentrations reaching 3650, 3050 and 1299 µg/kg d.w., respectively according to Eljarrat et al., (2001), followed by Po river in Italy (1800 µg/kg d.w), Nile river in Egypt (933 µg/kg d.w) and Abou Ali estuary in Lebanon (667.8 µg/kg d.w) (Table 3). Highest ∑PAHs concentrations reaching 210 000 and 610 000 µg/kg 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, etc.), 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 mean of ∑PAHs concentrations of samples collected from Adriatic Sea, Aegean Sea and Northwestern Mediterranean Sea were 19 - 426 µg/kg d.w, 148 µg/kg d.w. and 119 µg/kg 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 µg/kg d.w. (Baumard et al., 1998b) 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.

Table 3: Highest total concentrations of ∑PAHs (µg/kg d.w.) found in sediment samples collected from Mediterranean sites.

Studied sites	***Min. Concentration***	***Max. Concentration***	***N° PAHs***	***References***
Italy				
Naples harbour	9	31774	16	Sprovieri et al., 2007
Venice Lagoon	65	48000		La Rocca et al., 1996
Venice Lagoon	315	810		Frignani et al., 2003
Venice Lagoon	15.1	388.9		Parolini et al., 2010
Venice Lagoon	20	502		Secco et al., 2005
Pialassa Baiona	1000	135000		Vassura et al. (2005)
Pialassa Baiona	3030	87150		Guerra., 2011)
Mar Piccolo, Taranto	380	12750	16	Cardellicchio et al., 2007
Mar Piccolo, Taranto	100	180		Cardellicchio et al., 1989
Gulf of Taranto	1484	262446	16	Annicchiarico et al., 2011
Po River	100	1800		Viganò et al., 2003
France				
Ajaccio harbour, Corse		20440	26	Baumard et al., 1998a
Lazaret Bay	1440	48090	14	Benlahcen et al., 1997
Lazaret navy harbour		13010	14	Baumard et al., 1998a
Gulf of Lions	80.00	1500.00	11	Tolosa et al., 1996
Gulf of Lions	161.00	2176.00	21	Bouloubassi et al., 2012
Berre Lagoon	38	2323		Jacquot et al., 1999
Berre lagoon	334	853	16	Kanzari et al., 2012
Thau Lagoon	59	7679		Leaute., 2008
Rhone Delta	325	3182		Lipiatou and Saliot., 1991
Rhone River	1070	6330	15	Bouloubassi and Saliot., 1993
Gironde Estuary	18.5	4888	17	Budzinski et al., 1997
Spain				
Barcelona harbour	1740	8420		Baumard et al., 1998b
Barcelona harbour	300	10320	16	Martínez-Lladó et al., 2007
Besós River		1299		Eljarrat et al., 2001
Francolí River		3050		Eljarrat et al., 2001
Llobregat River		3650		Eljarrat et al., 2001
Greece				
Thermaikos Gulf	580	930		Kilikidis et al., 1994
Morocco				
Moroccan Coast	15	551	16	Pavoni et al., 2003
Turkey				
Izmit Bay	2500	25,000	14	Tolun et al. 2001
Izmit Bay	30000	1670000		Telli-Karakoç et al., 2002
Gemlik Bay, Turkey	50.8	13482	13	Ünlü and Alpar., 2006
Egypt				
Alexandria Harbour	8	131150	43	Mostafa et al., 2003
Alexandria Harbour	180	14100		Barakat et al., 2011
Nile Rive	305	933		Badawy and Emababy., 2010
Tunisia				
Sfax–Kerkennah coastal zone	113	10720	10	Zaghden et al., 2007
Bizerte Lagoon	83.3	447.1		Trabelsi and Driss., 2005

Bizerta Lagoon	1.5	2500		Louiz et al., 2008
Slovania				
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., 2015
Abou Ali Estuary		667.8	16	Merhaby et al., 2015

PCBs distribution in Mediterranean Basin

Harbors and industrial coastal areas are the most contaminated sites with PCBs in Mediterranean basins (Fig. 8b). Table 4 summarized the concentrations of ∑PCBs in sediments collected from some studied sites in Mediterranean countries. The highest levels of PCBs in the Northwestern Mediterranean sea were found in Cortiou near Marseille (France) with maximum concentration about 22900 µg/kg 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 µg/kg d.w. (Baldi et al., 1983) (Table 4). In Ionian Sea, PCBs contamination at Gulf of Taranto (Italy) is related to industrial sources and harbor activities with concentrations ranged from 85 to 1780 µg/kg 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 µg/kg d.w and 0.9 - 1211 µg/kg d.w., respectively (Table 4). Recently, a study has been conducted in the east of North Levantine Sea (Merhaby et al., 2015a,b) in Lebanese coast. The concentration of PCBs has been detected at high level reaching 1303 µg/kg 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 concentration 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 µg/kg d.w.) (Fernandez, 1991) (Table 4). In Adriatic Sea, PCBs pollution derives from Rijeka Bay in Croatia with maximum concentration reaching 597 µg/kg 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 µg/kg d.w. less than found at Keratsini harbour, Saronikos Gulf in Greece which showed also elevated levels about 4.78 - 351.8 µg/kg d.w. (Galanopoulou et al., 2005). In the Southwestern sub-basin, high concentrations (323 µg/kg 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 µg/kg d.w.) and inside Venice lagoons (6 - 1590 µg/kg 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 detecteded at Berre lagoon with concentrations ranging from 468.8 to 541.4 µg/kg d.w. (Kanzari et al., 2012) (Table 4).

The contribution of River inputs of PCBs pollution in Mediterranean Sea were observed at four Mediterranean countries; Spain, Italy, Lebanon and France (Fig. 8b). In Spain, the highest PCBs concentration reach 1772 µg/kg d.w. in the mouth of Ebro River (Fernández et al., 1999). While, other study conducted recently 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 µg/kg d.w. Another contribution was observed from Tiber River in Italy with maximum concentration of 770 µg/kg 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 µg/kg d.w. (Kanzari et al., 2012) followed by Rhone River at Fos Gulf with concentration reaching 416 µg/kg 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 about 339.4 µg/kg d.w. (Merhaby et al., 2015b).

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. In this study, The PCBs concentrations found in the open sea of some Mediterranean countries such as in Northwestern Mediterranean Sea, Provencal basin (2 – 3 µg/kg d.w.), and Catalan basin, Spain (4 - 11 µg/kg d.w.), and North Adriatic Sea, Italy (3.2 - 58 µg/kg d.w.), Tyrrhenian Sea (0.88- 1.3 µg/kg d.w.), Southwestern Sea, Algeria margin (9 µg/kg d.w.) and Ionian Sea, Albany (5 µg/kg 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 µg/kg d.w. Whereas, other background intervals ranging from 1 to 5 µg/kg d.w. and from 1.2 to 2.9 µg/kg 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 didn't have more information about the number of total PCBs congeners studied.

Table 4: Total concentrations of ∑PCBs (µg/kg 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
Croatia				
Rijeka Bay, coast	0.9	597		Picer et al., 1981 Picer and Picer., 1992)
Albany				
Adriatic coast	1	5		Koci., 1998
Lebanon				
Port of Beirut		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

Obviously, the number of hotspots 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 hotspot areas are 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 hotspot 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 of PAHs and PCBs were 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 considering these rivers as transit zones and hotspots areas contaminated by these targeted 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 latest 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 etc…) causing POPs desorption from sorbing matrix and dissolved phase to re-enter into the water column and the atmosphere (Asher et al. 2007; Yan et al. 2008; Garcia-Flor et al. 2009). The highest concentrations were 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 ∑PAHs (I) and ∑PCBs (II) in sediment harbors of some Mediterranean countries.

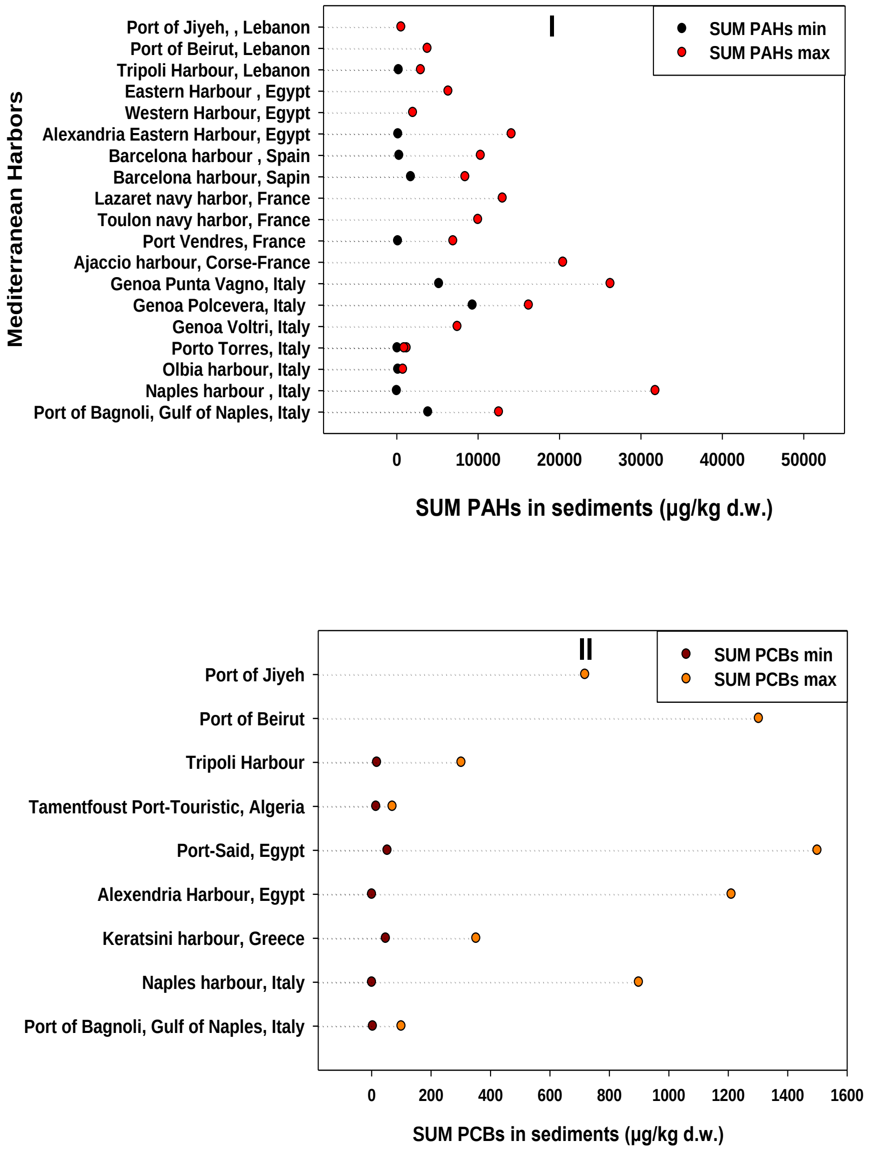


Fig. 9: Concentration of ∑PAHs (I) and ∑PCBs (II) in sediment harbors of some Mediterranean countries.

As shown in Fig. 9 for 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 for PCBs pollution were found in the following order 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 Mediterranean Sea some countries still used the equipment and/or other products containing PCBs such as in vessels and/or paints particularly in harbors. However, it is interesting to note that the Northwestern, the Adriatic and the Tyrrhenian sub-basins, South Levantine Sea and Agean 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 but 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 studied PAHs and PCBs congeners were not determined for all studies which 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.

Conclusion and Recommendations

Human has greatly modified the biosphere by the release a great amount of POPs into the environment. Multiples anthropogenic activities contribute to this pollution directly and indirectly whether by primary or secondary sources. Their physicochemical characteristics as a toxic, persistent, bioaccumulative dedicate 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 re-cycling 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 concentrations 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 established 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 sites in studied Mediterranean countries. Italy, France, Spain, Egypt and Turkey are the main countries contributed to PAHs and PCBs pollution in Mediterranean basin. 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 of the level of pollution by these targeted compounds at some sites due to the urbanization and industrialization reasons. Although, the technical and analytical development we have also a great lack in information related to open sea and deep sediment to take a definitive conclusion but we can suggest that Mediterranean Sea 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 measures 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 for 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 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.

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CHAPTER 2

SAMPLING AND ANALYSIS STRATEGY

II. Materials and Methods

II.1. Reagent and standards

II.1.1 Organic pollutants analysis

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

Organic targeted compounds

Sediments samples were analysed for 16 PAHs, 18 Me-PAHs, 28 PCBs including 12 dioxin-like PCBs (PCB-DL) and the 7 indicators PCB (PCBi) and 9 heavy metals. Table 6 summarized detailed information of the characteristics of individual PAHs, Me-PAHs and PCBs studied including numbers of aromatic rings and Chlorine atoms, qualifiers ions, quantifying ions, molecular weight and retention time. Targeted compounds were listed below:

PCBs (28 PCBs): 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209.

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

Me-PAHs (18 Me-PAHs) : 1-methylnaphthalene (1-MeNaph), 2-methylnaphthalene (2-MeNaph), 1,2-dimethylnaphthalene (1,2-DMNaph), 1,6-dimethylnaphthalene (1,6-DMNaph), 2,6-dimethylnaphtalene (2,6-DMNaph), 1-methylphenanthrene (1-MePhe), 2-methylphenanthrene (2- MePhe), 3-methylphenanthrene (3-MePhe), 9-methylphenanthrene (9- MePhe), 2-methylanthracene (2-MeAnthr), 1,7-dimethylphenanthrene (1,7-DMPhe), retene, 1-methylfluoranthene (1-MeFluo), 3-methylfluoranthene (3-MeFluo), 1-methylpyrene (1-MePyr), 4-methylpyrene (4-MePyr), 3-methylchrysene (3-MeChry), 6-methylchrysene (6-MeChry).

II.1.2. Inorganic pollutants analysis

All chemical reagents were ultrapure and analytical grade. All solutions were prepared using ultrapure water. Ultrapure water (Milli-Q) with 18.2 MΩcm^{-1} resistivity was produced by Millipore apparatus system. All of bottles, glassware and filtration equipment were systematically washed with nitric acid (10%) and then rinsed several times with Milli-Q water prior to use. Reagent blanks were included in each batch of analysis. Total heavy metal concentrations were expressed in µg/g dry sediments. A certified reference materials from the National Research Council of Canada (PACS-2, HISS-1 and MESS-3) was used as calibration standard material to validate the accuracy and precision of the analytical method. The recoveries of trace metals in standard materials with known concentrations were between 95 % and 105 %, which in general can be considered satisfactory.

Inorganic targeted compounds

Trace metals (9 heavy metals): As, Cd, Co, Cr, Mo, Pb, Ni, V and Zn.

II.2. Experimental procedures

The analytical methodologies of organic and inorganic pollutants analysis found at trace levels in various environmental matrices are very complex and quite difficult because these compounds presents in the complexity of the mixtures and they strongly bound to the matrix, thus the low detection limits are required (ppb to ppt) (Arslan-Alaton and Olmez-Hanci, 2013). During the last decades, new specific and sensitive methods were developed to prevent the analytical problems and reduce the quantity of organic solvents and the time required for sample preparation. These analytical methods involve the following steps: Extraction, clean-up or purification, separation and quantification.

The POPs in environmental matrices can be extracted by using various technique such as (i) Soxhlet extraction (SE), (ii) liquid-liquid extraction (LLE), (iii) ultrasonic-assisted extraction (UAE), (iv) microwave-assisted extraction (MAE), (v) accelerated solvent extraction (ASE) or pressurized liquid extraction (PLE), (vi) solid-phase extraction (SPE), (vii) supercritical fluid extraction (SFE*), (viii) subcritical water extraction (SWE), and (ix) matrix solid-phase dispersion (MSPD) (Ni et al., 2011; Xie et al., 2011). The selection of the appropriate analytical technique is an important step of quantification of POPs. The ASE is an interesting alternative to conventional Soxhlet procedure which is widely accepted as robust, since it reduces the extraction time one hour and solvent consumption (~ 30 ml with ASE versus ~300 ml with Soxhlet) (Eljarrat and Barcelo, 2003).

The clean-up or purification step is needed to eliminate the interfering compounds or co-extracted matrix. The Preparative liquid chromatography (LC), is the most common technique used for sample cleanup and is typically based on solid-liquid adsorption in open columns using silica-based sorbents and additional sorbents like Florisil; basic alumina and porous graphitic carbon are commonly used to fractionate the extracts in subgroups of analytes, which can be determined separately or mixed.

Following the extraction and Cleanup procedures, POPs are separated on gas chromatography (GC) coupled with mass spectrometry (MS), which allows the separation and purification of the individual compounds on the GC and introduces them separately to the MS where the specific mass spectra of each component will be measured. Due to its specificity and sensitivity, GC-MS techniques have been extensively applied to abiotic and biotic samples for POPs analysis (Arslan-Alaton and Olmez-Hanci, 2013). Fig. 10 shows the Analysis strategy of PAHs, Me-PAHs and PCBs adopted in this work and in the following sections they will be described briefly.

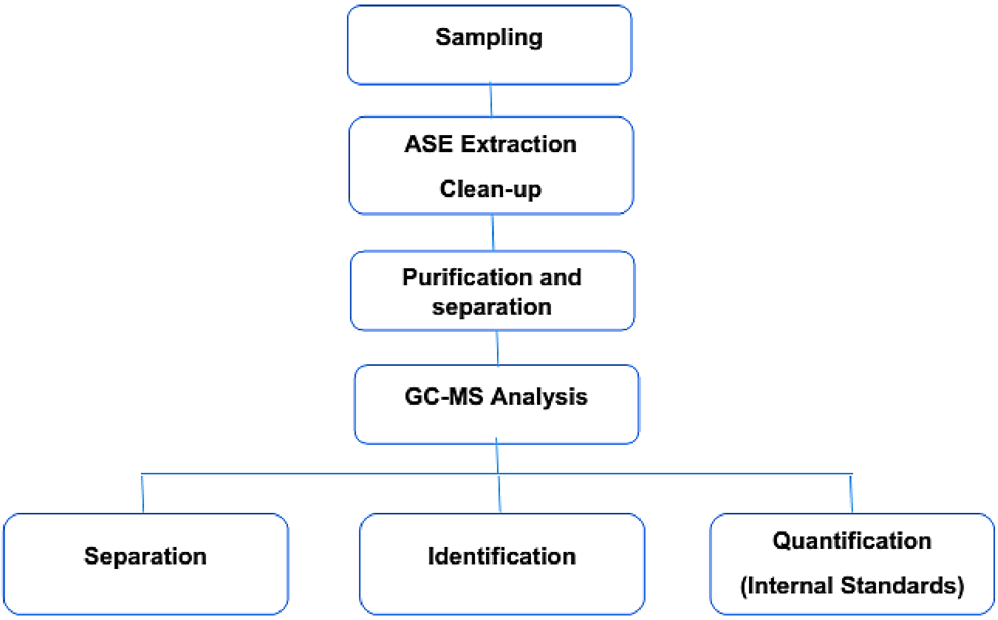

Fig. 10: Analysis strategy of PAHs, Me-PAHs and PCBs.

II.3. Studied Sites

Lebanese coast are being destroyed and replaced with beach resorts, large commercial facilities, industrial units and harbors (Zahreddine et al., 2004). This intensive anthropogenic activity is a potential source of coast pollution. The sampling stations were selected to cover Lebanese coastline zones (LCZ) with various industries and estuaries, particularly that influenced by intense shipping, freshwater input and touristic activities closed to several hotspots adjacent to the Lebanese coastline. These stations represents a wide range of environmental conditions in particular at ports, bays and estuaries where the accumulation of pollutants is enhanced in these semi-enclosed basins due to limited water exchange with the open sea (Okay et al., 1996; Karageorgis et al., 2002). The remobilization of coastal sediment has been identified as a key process capable of reintroducing contaminants like POPs and heavy metals to the water column which poses a potential risk to the wildlife ecosystem and human health (Jurado et al., 2007; Lohmann et al., 2007; Huang et al., 2011).

This assessment study covers about 110 km of Lebanese coastline extending from Jiyeh to Tripoli city (Eastern Mediterranean Sea, Lebanon). Thirteen surficial sediment samples were collected from six sampling stations including; the commercial Port of Tripoli and Beirut, the Port of Jieh Power Plant, Abou Ali estuary, Touristic resorts beach in Chekka bay, and Jounieh bay (Fig. 11). The GPS coordinates and other characteristics of the studied sites are presented in Table 5.

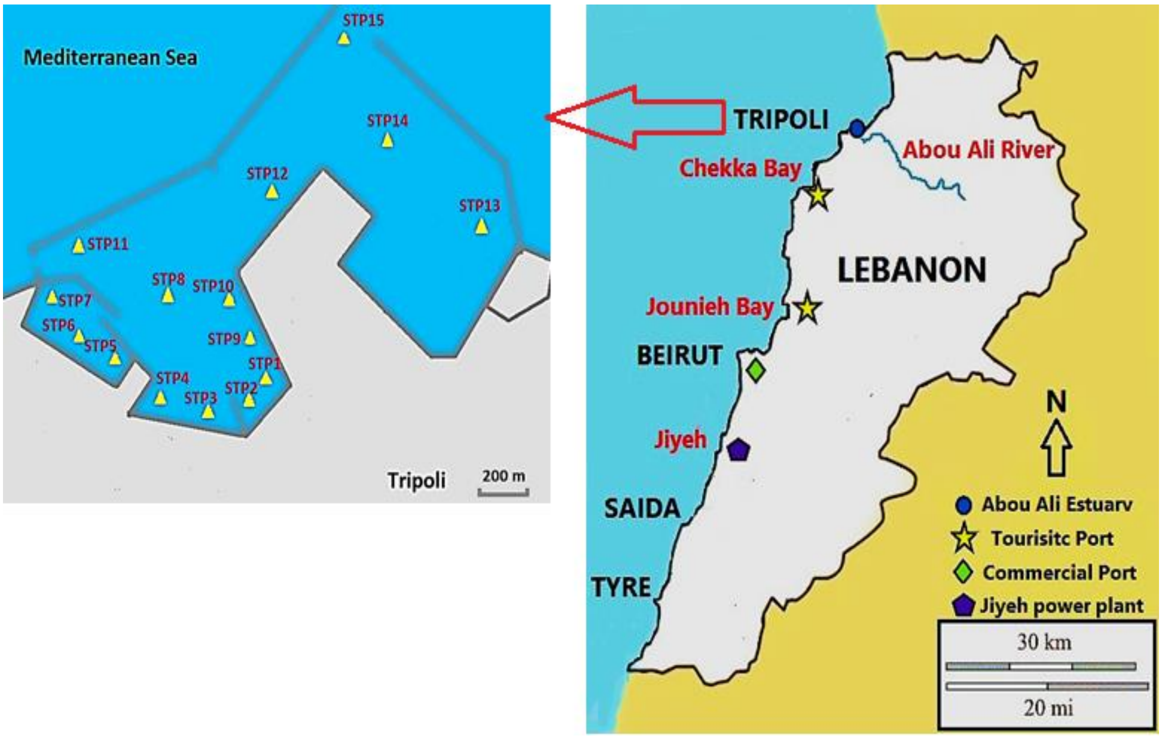

Fig. 11: Map of Studied Sampling Stations along LCZ.

Port of Beirut is the main important harbor in Lebanon and is one of the largest and busiest ports of the Mediterranean Sea due to its role in the maritime trade between East and West. It is located in the center of Lebanon and has been serving Capital of Beirut for shipping, transportation and fishery activities for the past several hundred years; the harbor covers an area of approximately 1.2 km^2.

Jiyeh power plant is located in Jiyeh city directly on the coastline at 30 kilometers south of Beirut. Its total area comprises around 40,000 m². The harbor activities are essentially reserved for petroleum products where the fuel supply to this power plant will continue to be by ship from the Mediterranean Sea.

In Chekka Bay, the samples were collected from a private beach resort located in Chekka costal city situated 65 km north of Beirut. This is affected by touristic activities and the presence of yachting center. Furthermore, the different levels and orientation of industrialization development in this area are due to the presence of multiple industries, in particular to two cement factories located about a hundred meters away. These conditions may allow to provide the interesting contrast for understanding pollutants source and distribution mechanisms in this marine ecosystem for our knowledge of the potential risk and actual danger to the human health. The samples were collected from this beach due to the difficulties to access to the basins of these factories. On the other hand, from Jounieh Bay, the samples were collected from a private beach also located in Jounieh costal city about 17.8 km north of the Beirut. This beach located on this natural bay hosts this city for touristic activities without the presence of any significant influence by industrial activities like the case of Chekka bay.

Abou Ali River in north Lebanon extends of 44.5 km long and its basin encompasses nearly 236 towns and villages where around 800,000 inhabitants live. The source is located at 1,850 m of altitude and the river falls to nearly sea level passing through Tripoli coastal plain. Indeed, Tripoli is the second largest Lebanese city with approximately 350,000 inhabitants making it highly affected by anthropogenic activities. The Abou Ali River catchment basin area is estimated at 484 km^2 of which 97 % is mountainous with average flow rates in dry season (October) and wet season (March) are approximately 0.8 m^3 s^{-1} and 17.2 m^3 s^{-1}, respectively (Massoud et al., 2006). The Tripoli coastal area receives approximately 369 Mm^3/year freshwater inputs from Abou Ali River (Kabbara et al., 2008), where the samples were collected from the estuary of this river on the Mediterranean Sea.

Table 5: Description of the sampling stations at Port of Tripoli basins and five other sites along LCZ.

Site name	Stations	Coordinates	Depth (m)	Description	
1th campaign in December 2013					
Port of Tripoli	SPT1	34°27'9.42"N 35°49'35.79"E	8	Old basin	Loading/unloading of scraps and Touristic vessels in the corner of old basin
	STP2	34°27'7.59"N 35°49'30.96"E	8	Old basin	Ships maintenance
	SPT3	34°27'5.61"N 35°49'22.72"E	2.5	Old basin	Sewage outfall in old basin
	SPT4	34°27'6.09"N 35°49'12.36"E	2.5	Old basin	Ships maintenance in old basin
	SPT5	34°27'12.26"N 35°49'5.49"E	1.8	Fishery basin	fishery basin
	SPT6	34°27'15.66"N 35°48'56.75"E	2	Fishery basin	fishery basin
	SPT7	34°27'22.85"N 35°48'52.74"E	1.8	Fishery basin	fishery basin
	SPT8	34°27'20.67"N 35°49'18.24"E	6	Old basin/Fishery basin	Mid of old basin and the entrance of fishery basin
	SPT9	34°27'15.53"N 35°49'31.50"E	8	Old basin	Loading/unloading of Cargos
	STP10	34°27'20.59"N 35°49'28.53"E	9.5	Old basin	Loading/unloading of Cargos
	SPT11	34°27'29.62"N 35°48'58.36"E	6	Old basin	Before breakwater of old basin

	SPT12	34°27'35.09"N 35°49'35.19"E	15	New basin	Future basin for container trade
	SPT13	34°27'28.96"N 35°50'18.56"E	16	New basin	Near landfill
	SPT14	34°27'45.37"N 35°50'0.86"E	16	New basin	Between new basin and landfill
	SPT15	34°28'0.08"N 35°49'49.64"E	16	New basin	Ships entrance
2nd campaign in May 2014					
Port of Jiyeh Power Plant	SPJ1	33°38'53.85"N 35°23'53.50"E	4	Commercial harbor	Shipping activities, loading/unloading of petroleum product.
	SPJ2	33°38'53.85"N 35°23'53.50"E	6		
	SPJ3	33°38'53.85"N 35°23'53.50"E	10		
Port of Beirut	SPB1	33°54'18"N 35°31'16"E	2	Commercial harbor	Loading/unloading of general cargos, container operations, shipping, transportation and fishery activities with the presence of three industrial buildings.
	SPB2	33°54'18"N 35°31'16"E	3		
	SPB3	33°54'18"N 35°31'16"E	5		
Jounieh bay	SJB1	33° 58' 59"N 35°38' 59" E	4	Touristic beach resort (marina)	Touristic activities including swimming, water sports, boating and fishing and yachting center.
	SJB2	33° 58' 59"N 35°38' 59" E	6		
	SJB3	33° 58' 59"N 35°38' 59" E	10		
Chekka bay	SCB1	34°20'4.01"N 35°43'25.75"E	3	Touristic beach resort (marina)	Touristic and industrial activities due to the presence of two cement factories located about hundred meters away from this beach.
	SCB2	34°20'4.01"N 35°43'25.75"E	4		
	SCB3	34°20'4.01"N 35°43'25.75"E	7		
Abou Ali estuary	SAE1	34°27'30.16"N 35°50'29.68"E	3	Estuary	Coastal sea receives approximately 369 Mm^3/year freshwater input from Abou Ali River mixed with urban and industrial wastewater directly discharged into river without treatment.
	SAE2	34°27'30.16"N 35°50'29.68"E	6		
	SAE3	34°27'30.16"N 35°50'29.68"E	9		

II.4. Sampling and storage

Two sampling campaigns were performed. (i) The first one was done in December 2013 at Tripoli Port where 15 superficial sediment samples (0-5cm) were collected from different stations. (ii) The second one, the sampling was conducted in May 2014, at Port of Jieh Power Plant, Port of Beirut, Jounieh bay, Chekka bay and Abou Ali estuary by expert diver using Glasses tubes properly disinfected. At each site, the sampling was done in triplicate. Fig. 11 presents the locations of these sampling sites and a brief description of their characteristics is reported in Table 5.

For POPs analysis, the samples were homogenized then transferred into pre-calcinated aluminum containers capped with aluminum foils. For heavy metal analysis, the samples were transferred into pre-washed polyethylene (plastic) bags to prevent any oxidation and avoid metal pollution of the samples. All the sediment samples were transported to the laboratory and treated directly of were frozen at -20 °C until the treatment and quantification of the contamination levels.

II.5. Sample treatments

The samples were dried at room temperature under laminar hood until reaching constant weight. The dried sediments were finely grinded to powder manually using an agate mortar. Sediment samples processing were first sieved at 224 μm to remove large particles and approximately 15 g of sieved sediment samples were spiked with internal standards A-d10, N-d10, Per-d12, Phe-d10 and Pyr-d10 for PAHs and Me-PAHs and TCN, PCB112 and OCN for PCBs quantification and homogenize the mixture. For trace metal analysis, in order to reduce the effect of sediment grain size on the variability of the physicochemical measurements, the particles with size less than 63 μm were collected and used for the extraction.

II.6. Sample extractions

II.6.1. Organic pollutants extraction

Spiked sediment samples were kept 12h for the equilibration. After a delay of equilibration, sediments were extracted using an accelerated solvent extraction (ASE 200, Dionex Corp., USA). The ASE conditions under which the extraction is carried out were described in Tronczynski et al. (2005). Briefly, the conditions of ASE extraction were: heated for 5 min, temperature 100°C, static solvent extraction time 2 min with 5 static cycles and two times, pressure 138 bars, purge 3 min and 35 % flush and high purity nitrogen was employed as the purge gas.

After the extraction, the molecular sulfur was removed by addition of activated copper to the extracts. The extracts were concentrated, solvent-exchanged to hexane, and were then purified and fractioned on a silica column to eliminate organic interferences (De Boer and Law, 2003). Targeted compounds were recovered by elution with 15 ml of hexane/dichloromethane mixtures (3/1 v/v) and then 10 ml of hexane/dichloromethane mixture (1/1 v/v) (Fraction 2). Fig. 13 presents the scheme of the analytical steps for the quantification of organic pollutants (left site) and ASE extraction (right site).

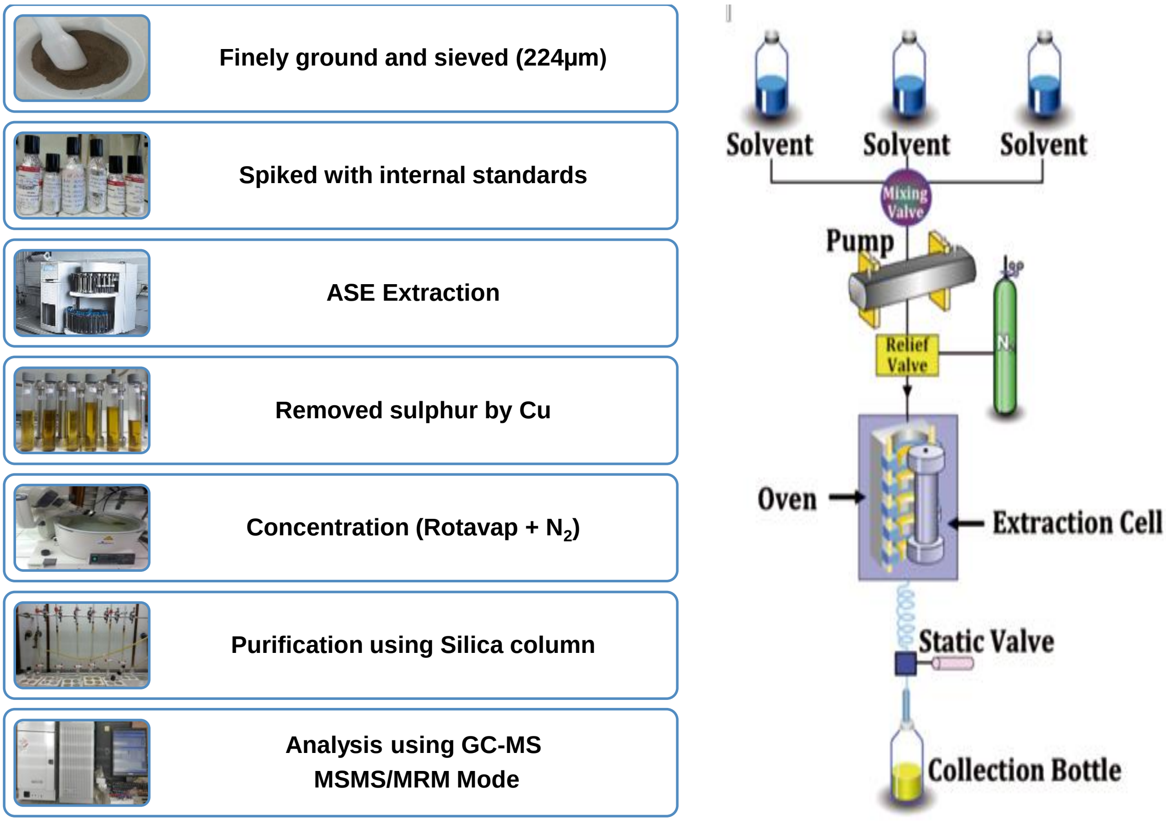

Fig. 12: Scheme of the analytical steps for the quantification of organic pollutants (left site) and ASE extraction (right site).

II.6.2. Inorganic pollutants analysis

The trace metals were analysed according to the protocol described by Ouddane (1990) and Lesven et al. (2010). For each extraction, about 200 mg of dry sediment sample or reference materials (PACS-2, HISSE-1 and MESS-3) was digested with a mixture of concentrated acids 6ml HF (40%)/ 6ml HCl (37 %)/ 2 ml HNO3 (65 %) (3:3:1 v/v/v) in Teflon tubes putted in heating bath at 100 °C for 24 h to mineralized the solid grains. Then, after evaporation, the samples were diluted to final volume of 20 ml with ultrapure water (Milli-Q). The solution was then filtered at 0.45 µm to eliminate the carbon residue (Lesven et al., 2010) and stored at 4 °C until analysis (Priadi et al., 2011). Fig.13 presents the scheme of the analytical steps for the quantification of trace metals in sediments.

In order to determine trace metals associated with the bioavailable fractions of sediment samples, which are considered as reactive fractions, the method developed by Huerta-Diaz and Morse (1990) has been used. About 200 mg of sediment was attacked with 20 mL of 1 M HCl during 24 h (37%) at room temperature with continuous agitation. After leaching, the solution was also filtered and stored at 4 °C until analysis (Fig.13). The individual concentrations of major and trace elements in the extracts were measured in samples using inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian, Vista-PRO axial view) or Inductively Coupled Plasma Masse Spectroscopy (ICP-MS, Thermo Electron Corporation, Element X7 Series).

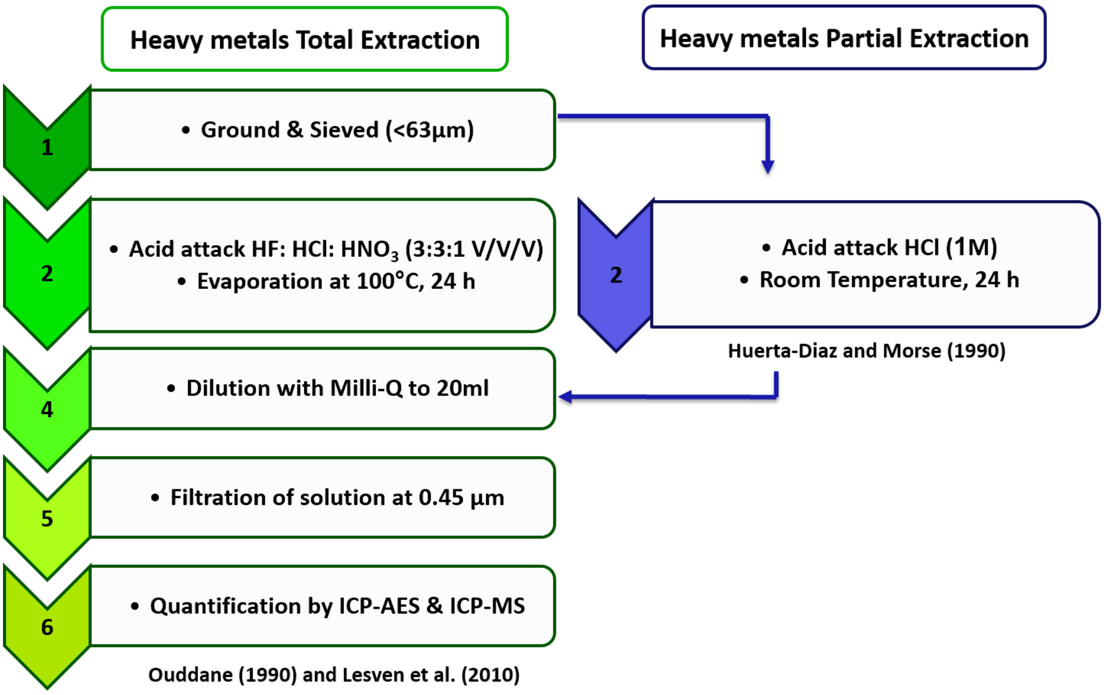

Fig. 13: Scheme of the analytical steps for the quantification of heavy metals in sediment samples.

II.7. Quantification

II.7.1. Organic pollutants quantifications: GC-MS analysis

PAHs, Me-PAHs and PCBs were analyzed using a Varian 3900 gas chromatograph (GC) equipped with a deactivated fused-silica guard column (5 m, 0.53 mm i.d.) and a fused-silica capillary Phenomenex XLB (60 m length, 0.25 mm i.d., 0.25 µm film thickness) and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS). The carrier gas was helium held at a constant flow rate of 1 mL/min. Each group of organic compounds was analyzed separately. The temperature of the GC oven was programmed as follows: from 70°C (1 min) to 170°C at 10°C/min, then to 230°C at 4°C/min, and then to 300°C at 3°C/min (13 min) for HAPs and Me-HAPs and from 80°C (1 min) to 170°C at 10°C/min, then to 230°C at 4°C/min, and then to 300°C at 3°C/min (19 min) for PCBs. Samples were injected in the splitless mode at 280°C and the injector was purged with helium after 1 min. The identification of each PAH, Me-PAH and PCB was done on the basis of the retention time and the mass spectrum from chromatogram of standard solutions acquired in full scan mode. The quantification was then performed in MS-MS mode for better selectivity. Response factors were determined relative to the internal standards response and to standard mixtures. The individual concentrations of PAHs, Me-PAHs and PCBs were calculated to give the total concentration of each studied contaminants in µg.kg^{-1} of dry weight (dw) of sediment. Table 6 presents the number of aromatic rings, qualifier ions, quantifying ions, retention time (RT) and other characteristics of individual targeted compound.

Table 6: Number of rings, qualifier ions, quantifying ions, retention time (RT) and other characteristics of individual PAHs, Me-PAHs and PCBs congeners selected in study.

18 Me- PAHs	*Nº of rings*	*Qualifier Ions (m/z)*	*Quantifying ions (m/z)*	*(RT, min)*	*16 PAHs*	*Nº of rings*	*Qualifier Ions (m/z)*	*Quantifying ions (m/z)*	*(RT, min)*
1-MeNaph	2	142	115, 116, 142	11.1	**Nap**	2	128	128, 126, 102	9.6
2- MeNaph	2	142	115, 116, 142	11.34	**Acy**	3	152	151,152,150	13.5
1,2-DMNaph	2	156	141,153	12.68	**Ace**	3	154	154,152	13.99
1,6- DMNaph	2	156	141,153	12.98	**Fl**	3	166	163,166,164	15.72
2,6- DMNaph	2	156	141,153	13.47	**Phe**	3	178	178,177,152	19.59
1- MePhe	3	192	189,192	21.88	**Ant**	3	178	176,178,152	19.82
2- MePhe	3	192	189,192,190	22	**Pyr**	4	202	201,202,203	25.47
3- MePhe	3	192	189,192	22.24	**Flu**	4	202	202,201,203	26.66
9- MePhe	3	192	189,192	22.39	**BaA**	4	228	226,227,229	34.09
2- MeAnthr	3	192	189,192,190	22.52	**Chr**	4	228	227,228,229	34.33
1,7- DMPhe	3	206	191,190	25	**BbF**	5	252	251,252,253	41.14
Retene	3	234	219,204	28.48	**BkF**	5	252	251,252,253	41.32
1- MeFluo	4	216	213,214,189	28.54	**BaP**	5	252	252,253,251	43.15
3- MeFluo	4	216	213,214,189	28.6	**IP**	5	276	275,276	49.74
1- MePyr	4	216	189,213,214	29.76	**DBA**	6	278	277,279,278	50.02
4- MePyr	4	216	189,214	29.94	**BgP**	6	276	275,276,277	51.24
3- MeChry	4	242	239,240	36.91					
6- MeChry	4	242	239,240	37.36					
28 PCBs	**Nº of Cl atoms**				**28 PCBs**	**Nº of Cl atoms**			
CB8	2	223	152,187,186	16.76	**CB138**	6	361	325,358,290	30.45
CB18	3	257	221,223,186,188	18.31	**CB126**	7	395	324,257,254	31.09
CB28	3	257	256,186,221	20.28	**CB170**	5	326	359,361,326,392	31.1
CB52	4	291	255,257,222,220	21.66	**CB128**	6	361	325,327,360,290	31.78
CB44	4	266	255,257,220,222	22.46	**CB157**	6	361	360,290	31.91
CB66	4	291	290,222,250	24.35	**CB156**	6	361	360,290	33.05
CB101	5	326	289,291,256	25.32	**CB169**	6	361	360,290	33.27
CB81	4	291	290,222	26.44	**CB180**	7	395	359,394,361,324	33.78
CB77	4	291	290,222,220	27.13	**CB167**	7	395	360,290	35.02
CB123	5	326	324,256,255	28	**CB187**	6	361	359,361,394,324	35.22
CB118	5	326	324,256,255	28.2	**CB189**	7	395	394,326,325	36.81
CB114	5	326	324,256,255	28.68	**CB195**	8	430	394,395,426	37.37
CB153	6	361	325,358,290	29.15	CB206	9	464	428,429,460,394	40.29
CB105	5	326	324,256	29.42	CB209	10	499	500,428,497	41.81

II.7.1. Quantification of trace metal elements

The individual concentrations of trace elements in the extracts were measured in samples using inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian, Vista-PRO axial view) or Inductively Coupled Plasma Masse Spectroscopy (ICP-MS , Thermo Electron Corporation, Element X7 Series) (Fig.14). Mixed standard solution of ten trace metals was used to prepare etalon solutions with croissant concentrations (0.5, 1, 5, 50 &100 ppm) and individual standards solution for PO_4^{3-} (1000 ppm), Ca (1000 ppm) and S (50 and 100 ppm) was also used to obtain an accurate results by ICP-AES, Varian, Vista-PRO axial view). ICP-MS was used for the lower concentrations determination (<10µg/l).

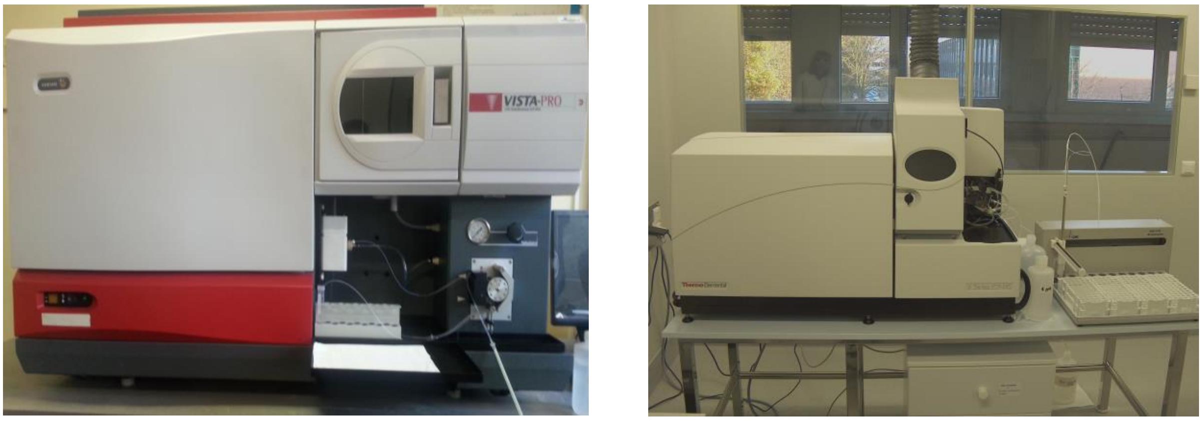

Fig. 14: ICP-AES and ICP-MS used for heavy metals quantification.

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CHAPTER 3

RESULTS AND DISCUSSION

Article 1

ORGANIC POLLUTION IN SURFICIAL SEDIMENTS OF TRIPOLI HARBOUR, LEBANON

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Marine Pollution Bulletin 93 (2015) 284-293

Date

22-01-2015

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Marine Pollution Bulletin 93 (2015) 284–293

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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Baseline

Organic pollution in surficial sediments of Tripoli harbour, Lebanon

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Abstract

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

Keywords: Sediments, Harbour, PAHs, Me-PAHs, PCBs, SQGs.

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

PAHs and Me-PAHs are widely spread chemical pollutants released into the environment. They can be originated either from natural processes including biomass burning, volcanic eruptions and diagenesis (Wang et al., 2007), and from anthropogenic inputs such as fuels or oil spills and their incomplete combustion. Anthropogenic origins are generally the major sources of PAHs pollution in the environment (Pascale et al., 1998; Yunker et al., 2001; Chen et al., 2013; Acquavita et al., 2014; Mirza et al., 2014). PAHs can enter water surface as a mixture origin via atmospheric deposition, water run-off, municipal and industrial effluents, sewage outfalls, oil spillage and maritime transport (Maher and Aislabie, 1992; Manoli and Samara, 1999; Zhou et al., 2003). In the case of sediment resuspension, some PAHs in water could adsorb on the sediment particles and flocculate, leading to an accumulation of PAHs in sediment (Feng et al. 2012). Due to their mutagenic and carcinogenic properties, 16 PAHs are listed as priority pollutants by the US Environmental Protection Agency (USEPA) (Keith and Telliard, 1979; Conney, 1982; Connel et al., 1997; Straif, 2005; Cardellicchio et al, 2007; IARC, 2010, Tobiszewski and Namiesnik., 2011). The emission sources of hydrocarbons can be determined using different diagnostic ratios (Tobiszewski and Namiesnik., 2011; Yunker et al., 2002; Yunker and Macdonald, 1995).

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

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

PAHs and PCBs are characterized by their hydrophobic properties which allow their adsorbing with suspended particulate matter (SPM) and finally deposited in the sediment which constitutes a reservoir (Brownawell and Farrington., 1986; Zhou and Rowland, 1997; Glynn et al., 1995; Taklin, 1996; Zhou et al., 1996, 1998, 2000 ; Zhou et al., 2002; Manoli and Samara., 1999; Jones and Voogt., 1999; Nemr and Abd-Allah., 2003; Page et al., 1999). Contaminated sediments become an important source of pollution and can pose significant threat to aquatic organisms and humans health (Wernersson et al., 2000; Del Valls et al., 2004), particularly when sediments are disturbed or dredged. High bioavailability of PCBs occurred frequently in harbour areas due to the intensive shipping and dredging activities (Eggleton and Thomas, 2004; Nikolaou et al., 2009). Indeed, harbours are critical areas where can concentrate and release a large amount of POPs into environment, due to intensive shipping activities and maritime transport. The ports are very complex systems, influenced strongly by anthropogenic activities. These include urban, surrounding industrial activities or installations that do not necessarily belong to the port (Darbra et al., 2004, Ruggieri et al., 2011). However, recent studies about organic contamination are concentrated only on the northwestern part of the Mediterranean Sea (Lipiatou et al., 1997; Dachs et al., 1999) and there are great lacks of information on the Eastern part (Gogou et al., 2000).

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

Sediments samples were analyzed for 16 PAHs, 18 Me-PAHs and 28 PCBs including 12 dioxin-like PCBs (PCB-DL) and the 7 indicators PCB (PCBi). Mixed standard solutions of PAHs and Me-PAHs were purchased from Restek Corp (Bellefonte, PA, USA). PCBs standard solution was obtained from Accustandard Inc. (New Haven, CT, USA). Tetrachloronaphtalene (TCN), 2,3,3',5,6-tetrachlorobiphenyl (PCB112) and octachloronaphtalene (OCN), used for PCB quantification, were purchased from Dr Ehrenstorfer (Augsburg, Germany). Deuterated internal standards for PAHs and Me-PAHs (acenaphthene-*d*10 (A-*d*10), naphtalene-*d*8 (N-*d*10), perylene-*d*12 (Per-*d*12), phenanthrene-*d*10 (Phe-*d*10) and pyrene-*d*10 (Pyr-*d*10)) were provided by LGC-Promochem (Middlesex, UK). HPLC-grade solvents (hexane, dichloromethane, methanol and acetone) were purchased from Dislab (France). No significant amount of targeted analytes was showed in procedural blanks. Ultrapure water (Milli-Q) was produced by a Millipore apparatus with 18.2 $M\Omega.cm^{-1}$ resistivity. Merck silica gel 60 (70-230 mesh ASTM) activated at 450°C was heated at 120°C for 12h prior to use. Glassware was systematically washed with detergent (Decon, East Sussex, UK), rinsed with ultrapure water and acetone and finally dried at 120°C prior to use.

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

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

In fact, no data are available about the organic contamination in this area and our study is the first. 15 sediment samples were collected from three semi-enclosed basins in Tripoli harbour (Mediterranean Sea, Northern Lebanon). The sampling sites are presented in figure 15. These sampling sites have a scarce water circulation and strongly influenced by harbour, fishery and municipal activities and their characteristics are presented in Table 7.

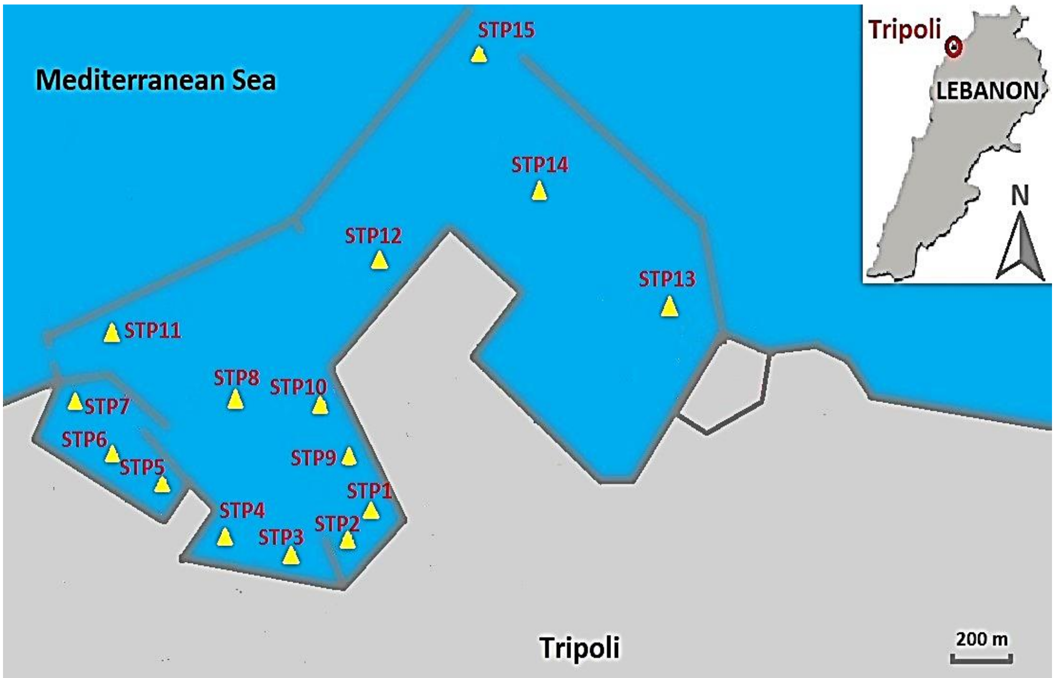

Fig. 15: Location of sampling stations in Tripoli Harbour basins, Lebanon.

Table 7: Description of sampling stations in Tripoli Harbour basins.

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

SPT14	34°27'45.37"N	35°50'0.86"E	16	New basin	Between new basin and landfill
SPT15	34°28'0.08"N	35°49'49.64"E	16	New basin	Entrance of ships

Sediments were collected in December 2013 at harbour Basins (Fig. 15). Superficial sediments samples (0-5 cm) were collected by diver using Glasses tubes properly disinfected. Each sample was homogenized before being transferred into pre-calcinated aluminium containers capped with aluminium foils. Sediment samples were transported in the laboratory and were frozen at -20°C then dried at room temperature in a laminar hood.

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

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

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

Me-PAHs (18 Me-PAHs) : 1-methylnaphthalene (1-MeNaph), 2-methylnaphthalene (2-MeNaph), 1,2-dimethylnaphthalene (1,2-DMNaph), 1,6-dimethylnaphthalene (1,6-DMNaph), 2,6-dimethylnaphtalene (2,6-DMNaph), 1-methylphenanthrene (1-MePhe), 2-methylphenanthrene (2- MePhe), 3-methylphenanthrene (3-MePhe), 9-methylphenanthrene (9- MePhe), 2-methylanthracene (2-MeAnthr), 1,7-dimethylphenanthrene (1,7-DMPhe), retene, 1-methylfluoranthene (1-MeFluo), 3-methylfluoranthene (3-MeFluo), 1-methylpyrene (1-MePyr), 4-methylpyrene (4-MePyr), 3-methylchrysene (3-MeChry), 6-methylchrysene (6-MeChry).

Sediment samples were dried under hood, then finely ground and sieved at 224 µm. Approximately 15 g of sieved sediment samples were spiked with internal standards A-*d10*, N-*d10*, Per-*d12,* Phe-*d10* and Pyr-*d10* for PAHs and Me-PAHs and TCN, PCB112 and OCN for PCBs quantification. After a delay of equilibration, sediments were then extracted using an accelerated solvent extraction (ASE 200, Dionex Corp., USA). The ASE conditions under which the extraction is carried out were described in Tronczynski et al. (2005). Briefly, the extraction conditions were heat 5 min, temperature 100°C, static solvent extraction time 2 min with 5 static cycles and two times, pressure 138 bars, purge 3 min and 35 % flush and high purity nitrogen was employed as the purge gas.

After the extraction with ASE, molecular sulfur was removed by addition of activated metallic copper to the extracts. The extracts were concentrated, solvent-exchanged to hexane, and were then purified and fractioned on a silica column to eliminate organic interferences (De Boer and Law, 2003; Jeanneau, 2007). Targeted compounds were recovered by elution with 15ml of hexane/dichloromethane mixtures (3/1 v/v) and then 10ml of hexane/dichloromethane mixture (1/1 v/v) (Fraction 2). Each fraction was concentrated using a rotary evaporator followed by a slight stream of nitrogen.

PAHs, Me-PAHs and PCBs were analyzed using a Varian 3900 gas chromatograph (GC) equipped with a deactivated fused-silica guard column (5 m, 0.53 mm i.d.) and a fused-silica capillary Phenomenex XLB (60 m length, 0.25 mm i.d., 0.25 µm film thickness) and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS). The carrier gas was helium held at a constant flow rate of 1 mL/min. Each group of organic compounds was analyzed separately. Temperature of the GC oven was programmed as follows: from 70°C (1 min) to 170°C at 10°C/min, then to 230°C at 4°C/min, and then to 300°C at 3°C/min (13 min) for HAPs and Me-HAPs and from 80°C (1 min) to 170°C at 10°C/min, then to 230°C at 4°C/min, and then to 300°C at 3°C/min (19 min) for PCBs. Samples were injected in the splitless mode at 280°C and the injector was purged with helium after 1 min. Identification of each PAH, Me-PAH and PCB was done on the basis of the retention time and the mass spectrum from chromatogram of standard solutions acquired in full scan mode. Quantification was then performed in MS-MS mode for better selectivity. Response factors were determined relative to the internal standards response and to standard mixtures. The individual concentrations of PAHs, Me-PAHs and PCBs were calculated to give the total concentration of each studied contaminants in µg.kg^{-1} of dry weight (dw) of sediment.

Individual concentration of targeted PCB, PAH and Me-PAH n sediment samples collected from 15 stations of Port of Tripoli basins are presented in Table 8.

Table 8: Individual concentration of PCB, PAH and Me-PAH in µg.kg-1 d.w. for 15 sediment samples in Tripoli harbour, Lebanon.

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

"-": not detected.

Total concentration of PAHs ($\sum_{16}$PAHs) in sediment samples collected from Port of Tripoli basins ranged from 243 to 2965 µg.kg^{-1} dw, with average value of 1061 µg.kg^{-1} dw.The highest concentration of $\sum_{16}$PAHs was observed at station STP6 collected from fishery basin with concentration ($\sum_{16}$PAHs) reaching 2965 µg.kg^{-1} dw sediment (Fig.16). Highest concentrations were observed in STP1, STP3 and STP4 with $\sum_{16}$PAHs reaching 2727, 1641 and 1964 µg.kg^{-1} dw respectively. Large variation of concentration was observed. This variation indicates the influence of Tripoli basins by multiple sources of PAHs may can be produced by fishery activities (STP5 and STP6), harbour activities such as ship maintenance (STP4) and urban discharges (STP3). Low $\sum_{16}$PAHs were detected at 243 µg.kg^{-1} dw, at STP13 closed to landfill. Concerning the substituted PAHs, the total concentration of $\sum_{18}$Me-PAHs in sediment samples varied between 54 and 1639 µg.kg^{-1} dw, with average value 498 µg.kg^{-1} dw. The highest concentration was found at STP4 located closed to ship maintenance area with concentration reached 1639 µg.kg^{-1} dw. Lower concentration was detected at STP14 collected from the mid of new basin between ship entrance/exit and landfill with concentration 54.2 µg.kg^{-1} dw. Concentration increase from STP15 (collected from new basin entrance/exit of ships close) to open sea reached 279 µg.kg^{-1} dw. Highest concentrations of $\sum_{18}$Me-PAHs were detected in STP1, STP2, STP4, STP6 and STP10 with respectively 725, 726, 614, 1638 and 649 µg.kg^{-1} dw (Fig.16). The Me-PAHs contamination of old basin of harbour and fishery basin could be originated from oil spills accidents during ships maintenance and oil leakage during oil supply for fishery boats.

Amongst 28 PCBs studied, 24 PCBs congeners (PCBs 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 157, 169, 170, 180, 187, 206, and 209) were detected and quantified in superficial sediments samples collected from Port of Tripoli basins. Three PCBs (101, 153, 138) were detected in all sediment samples and 4 PCBs (156, 167, 189 and 195) were under limit of quantification. The total concentrations of PCBs ($\sum_{28}$PCBs) were ranging from 17.9 to 301.9 µg.kg^{-1} dw. The highest concentration was detected at STP1 (301.9 µg.kg^{-1} dw) on the corner of old basin where occurred loading/unloading of cargos (eg., scraps), touristic vessels, urban discharges and ship maintenance activities. The lowest $\sum_{28}$PCBs was determined for STP5 collected from fishery basin with concentration reaching 17.9 µg.kg^{-1} dw. Other sampling sites, $\sum_{28}$PCBs were present at the level between 19.6 (STP14) and 91.4 µg.kg^{-1} dw (STP2).

These 28 PCBs included 7 PCBs congener's indicators ($\sum_{7}$PCBi _i.e. CB 28, 52, 101, 118, 138, 153 and 180), which are the most frequently detected in the environment and 12 high toxicity and persistent PCBs called PCBs dioxin-like (Σ12PCB-DL _ i.e. CB 77, 81, 105, 114,118, 123, 126, 156, 157, 167, 169, and 189). $\sum_{7}$PCBi detected in our sampling sites ranged from 11.6 and 127.3 µg.kg^{-1} dw with mean value of 30.4 µg.kg^{-1} dw. PCB-DL with highly toxic and persistent in the environment (Kimbrough et al., 2010; Tanabe and Minh, 2010) which can cause toxic effect particularly in endocrine system (Schantz, 1996; Rice and Hayward, 1997) were also detected in ours sediment samples. Σ_{12}PCB-DL varied between 1.4 and 111.2 µg.kg^{-1} dw with mean value of 12.4 µg.kg^{-1} dw. The average concentration of Σ_7PCBi represents 55.2 % while the Σ_{12}PCB-DL represents 22.6 % of Σ_{28}PCB. The highest concentration of Σ_7PCBi and Σ_{12}PCB-DL were observed in STP1 with concentration reaching Σ_7PCBi = 127.3 µg.kg^{-1} dw and Σ_{12}PCB-DL = 111.2 µg.kg^{-1} dw respectively. These results show that PCBs contamination detected in old basin of Tripoli harbour may be due to the presence of different sources of pollution.

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

Figure 16 shows, the Σ_{16}PAHs, Σ_{18}Me-PAHs, Σ_{28}PCBs, Σ_7PCBi and Σ_{12}PCB-DL concentrations for all sediments samples in Tripoli harbour basins.

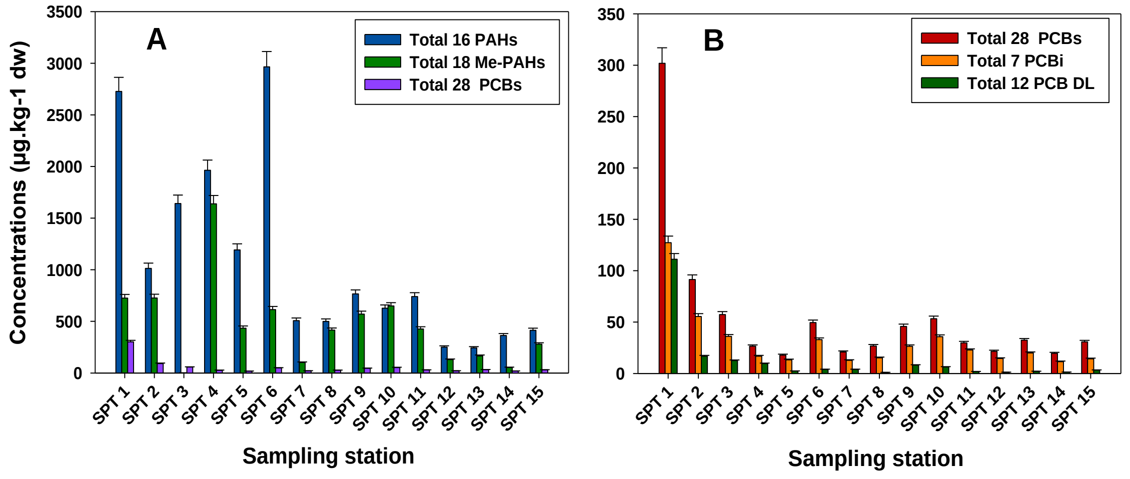

Fig. 16: Σ16PAHs, Σ18Me-PAHs, Σ28PCBs, Σ7PCBi and Σ12PCB-DL concentrations in Tripoli Harbour basins.

Most PAHs were detected and quantified in all samples except for station STP4. Dominance of high molecular weight PAHs with 4-rings (Pyr, Fluo, BaA, Chry) and 5-rings (BbF, BkF, BaP, DahA) were detected with 38.18% and 42.68% respectively (Fig. 17). The 2- and 3-rings PAHs represent only 0.92% and 12.50% respectively, due to their higher water solubility and their lower stability towards biodegradation process (Quantin et al., 2005). No significant variation was observed for the composition of Me-PAHs between 2-, 3- and 4-rings. The average compositions were 32.71%, 34.47% and 32.82% respectively for 2-, 3- and 4-rings Me-PAHs. It is interesting to note that lower molecular weight of PAHs (2 and 3-rings structures) are produced from petroleum products, fossil fuels and biomass incomplete combustion at low to moderate temperature and natural digenesis, while high molecular weight of PAHs (4- or more rings structures) are produced at high temperature (Yuan et al., 2001; Mai et al., 2002). In our sediment samples, the predominance of high molecular weight compounds with 4-rings or more were detected in all samples (Fig. 17).

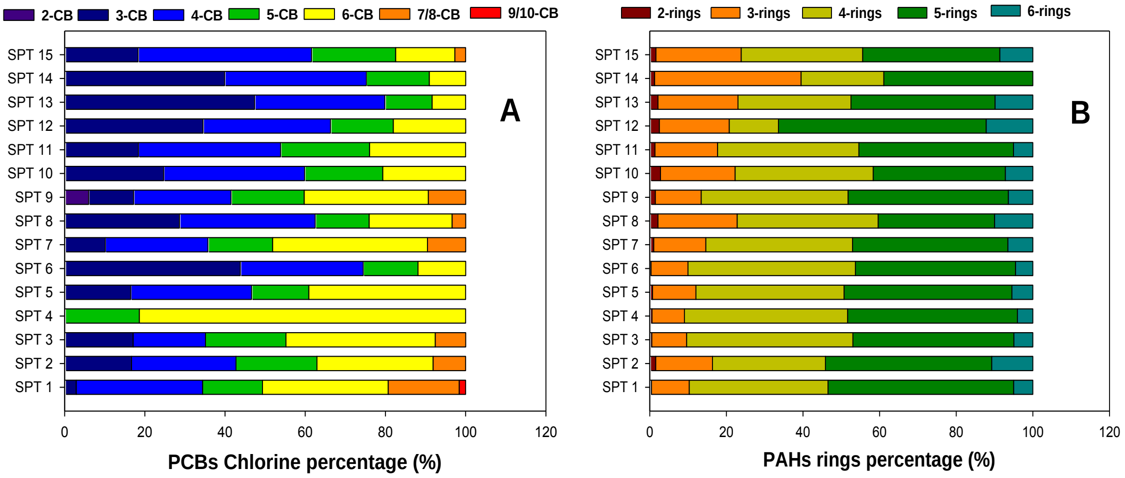

Fig. 17: PCBs and PAHs composition profile in the sediment samples collected from Tripoli Harbour.

Each PCBs congener has different biological activity and toxicity due to the number and position of chlorine atoms in the molecular structure. In addition to toxic effect exert by PCB-DL mentioned previously; also, neurotoxic effects have been observed for the ortho-substituted congeners, with two or more ortho-chlorines (Rice and Hayward. 1997; Schantz, 1996). The composition of the PCBs congeners from Tripoli Port sediments was dominated by the content of 4 and 6 Cl CB with 29.35% and 28.56% respectively (Fig. 17). Therefore the abundance of higher-chlorinated congeners indicates that anthropogenic pollution has influenced the Port of Tripoli basins (Hong et al., 2005; Mai et al., 2005). Due to high solubility and volatility of lower chlorinated congeners, transport via surface runoff and atmospheric processes of these compounds can be occurred easily. Also, during their transport in the atmosphere these congeners can be degraded by hydroxyl radicals (Mandalakis et al., 2003). Therefore, only small amount of lower chlorinated congeners deposit into marine sediments (Jonsson et al., 2003), which lead to higher level of high chlorinated PCBs congeners in the marine sediments. In our case, the percentages of 5Cl and 6Cl CBs represent 16.8 and 28.6 % respectively; and 3Cl and 4Cl reached 15.6 % and 29.4 % respectively (Fig. 17). These results suggest the presence of multiple sources of PCBs pollution in Port of Tripoli basins. The higher chlorinated PCBs can be due to the atmospheric deposition unintentionally released from port equipment, generators, ships, vehicles and trucks exhaust (Brož et al., 2000; Hong et al., 2005; Aries et al., 2006; Shibamoto et al., 2007; Liu et al., 2009). Also, the minor contribution of urban discharges, surface water runoff, harbour activities (e.g., ships maintenance) can be demonstrated by the presence of lower chlorinated PCBs in Port basins.

In general, anthropogenic PAHs are emitted as a mixture into environment (Tobiszewski and Namiesnik, 2011), which can be attributed to petrogenic and/or pyrogenic sources. Pyrogenic process responsible of PAHs inputs characterized by abundance of high molecular weight PAHs and parent PAHs (non-alkylated PAHs). The petrogenic process is characterized by high abundance of low molecular weight and alkylated PAHs (Baumard et al., 1997; Yuan et al., 2000). In this study, five molecular diagnostic ratios involve pairs of PAHs and Me-PAHs with the same molar mass and similar physicochemical properties (Ant/(Ant + Phe), Flu/(Flu + Py), BaA/ (BaA + Ch), C0/(C0+C1) P/A and C0/(C0+C1) F/P) are used for the identifying pollution emission sources contributing to PAHs released in Tripoli Harbour basins (Yunker et al., 2002; Tobiszewski and Namiesnik., 2011; Yunker et al., 2012).

For mass 178, Ant/(Ant + Phe) <0.10 suggests pollution of petroleum origin, while a ratio >0.10 indicates a dominance of combustion (Budzinski et al., 1997; Yunker et al., 2002; Liu et al., 2008). For mass 202, Flu/(Flu + Pyr) < 0.40 is consistent with petroleum inputs; a value between 0.40 and 0.50 indicates liquid fossil fuel (vehicle and crude oil) combustion and a ratio >0.50 indicates grass, wood, or coal combustion (Budzinski et al., 1997; Yunker et al., 2002). For mass 228, BaA/ (BaA + Ch) suggested that ratio <0.20 indicates petroleum inputs, a ratio between 0.20 and 0.35 indicates a mixed sources (either petroleum or combustion), and a ratio >0.35 indicates combustion sources (Yunker et al. 2002, 2012). Also, for homologues alkyl PAHs ratios C0/(C0+C1) P/A <0.5 indicates petroleum or combustion sources and a ratio >0.50 indicates coal or wood combustion or urban aerosols (Simo et al., 1997). For C0/(C0+C1)F/P <0.5 indicates petroleum sources and a ratio >0.50 indicates combustion sources (Yunker et al. 2002, 2012).

The results showed that the combustion of biomass (wood and grasses) and coal was the predominance source of PAHs contamination of Tripoli Port sediments. Two examples of cross plot of various ratios are showed in figure 18. The deposition of coal dust generated during the loading/unloading and storage of coal into Port of Tripoli are the major origins (Fig. 18). Moreover, the predominance of high molecular weight (HMW) confirms the origin of PAHs resulting from combustion process such as engine emissions from port equipments, maritime transport, vehicles traffic (highway) and diesel trucks (Transit activities) (Mostert et al., 2010; Tobiszewski and Namieśnik., 2012; Feng et al., 2012). Although, these results suggest the predominance of pyrogenic sources of PAHs contamination but we cannot ignored PAH derived from shipping activities, including ship discharges (ballast and/or bilge water) and oil spills in harbour basins. However, PAHs released by petrogenic sources are characterized by LMW which are preferentially biodegraded and dissolved compared to HMW derived from combustion and are preferentially adsorbed to particulate matter than deposits into sediments (Nemr and Abd-Allah., 2003). These characteristics lead to greater concentration of HMW in sediments than LMW and thus the predominance of PAHs derived from combustion sources.

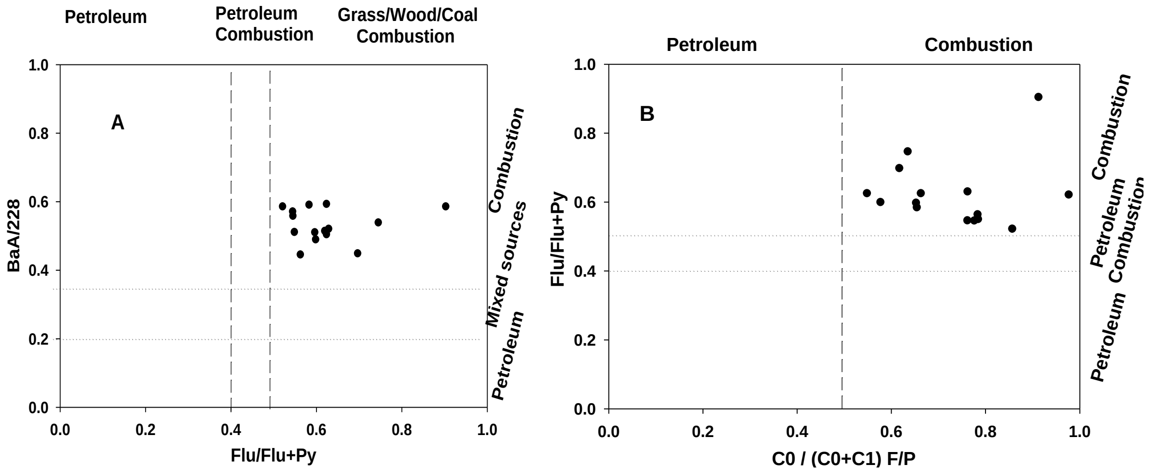

Fig. 18: **(A)** Cross plots of Flu/Flu+Pyr vs BaA/228, **(B)** C0/C0+C1 F/P vs the Flu/Flu+Pyr.

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

Indeed, atmospheric POPs derived from combustion can enter the surface water directly by gaseous exchange across the air/water interface, dry deposition of airborne particulate matter, by rainfall, and transported by storm water runoff (Hoffman et al., 1984, 1985; Dickhut and Gustafson, 1995; Dickhut et al., 2000; Tsai et al., 2002; Oros et al., 2006) so we suggest that the direct and indirect inputs of POPs affect their distribution in sediments samples of Tripoli

Harbour. In addition, due to their hydrophobic properties (low water solubility Kow (PAHs) = 10^{-7} to 10^{-10} mol/m^3) and strong affinity for organic matter (Culotta et al., 2006; Acquavita et al., 2014) POPs tend to accumulate in fine grained sediments. For our case, a geotechnical investigation Report was prepared for Tripoli Harbour by (Hatem, S., 2002) shows that the sediments types within old basin are consisted an approximately 7 to 10 meter thick layer of clayey sand to sandy clay with gravel and pebbles sometimes cemented (conglomeratic). For the new basin sediments are consisted of dark, greenish, grey, stiff to very stiff calcareous silty clay to clayey silt (marl) and traces of organic materials and peat were identified. Along principal breakwater, an approximately 5 meter thick layer of calcareous silty sand to clayey sand with gravel and pebbles sometimes cemented (conglomeratic) underlying by an approximately 5 meter thick layer of soft to medium stiff brown sandy to silty clay with gravel. The clay content in Tripoli harbour sediments is on the order of or greater than 30%. Therefore, we suggest also that the quite random distribution and concentration of POPs in Tripoli harbour sediments mainly can be due to the adsorption of POPs in the small particles (clay), which have a greater capacity of adsorption due of their greater specific surface area (Xia and Wang, 2008). Also, the shipping and maritime activities can lead to water and sediment movement and the remobilization of these pollutants influenced this distribution.

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

For Tripoli Port sediment, the total PAHs concentration ($\sum_{12}$PAHs) was observed exceeded TEL values at 6 samples (40% of total samples) (Table 9) but still below PEL value. Therefore, the biological adverse effects of PAHs that are expected occasionally for these samples collected from fishery basin and old basin of harbour closed to sewage outfall and ship maintenance areas. For others samples, the biological adverse effects are expected rarely with $\sum_{12}$PAHs are not exceeded TEL values. The total of PAHs concentrations ($\sum_{12}$PAHs) for all samples are below ERL were the biological adverse effects are rarely expected. Moreover, the classification of PAHs pollution levels which include low, moderate, high, and very high pollution levels when the concentrations of total PAHs are 0-100 ng/g, 100-1000 ng/g, 1000-5000 ng/g, and >5000 ng/g respectively (Baumard et al., 1998; Rahmanpoor et al., 2014). Based on this classification, sediment samples from Tripoli harbour basins varied between 243 and 2965 µg.kg^{-1} dw; so we suggest that it could be considered as moderate to high polluted with PAHs.

Total PCBs concentration (Σ_{28}PCBs) was exceeded TEL values at 11 samples (73% of total samples) (STP 1, STP2, STP3, STP4, STP6, STP8, STP9, STP10, STP11, STP13 and STP15) (Table 9), but still below PEL except for STP1 (Table 9). Therefore, the biological adverse effects of PCBs that are expected occasionally for the overall of Tripoli Port basins. In 1990, Maritime Navigation and Ports Authority of France was established « Géode » classification (Groupe d'Etude et d'Observation sur le Dragage et l'Environnement) for dredged materials in ports sediments. Therefore, based on this classification all samples sediments in Tripoli harbour basins were below N1 level (500 µg.kg^{-1} dw) which suggest that no environmental problems related to PCBs during dredged activities (Caplat, 2001).

Table 9: ∑12PAHs and ∑28PCBs obtained from 15 stations in Tripoli Port compared to TEL/PEL and ERL/ERM values.

Samples	**$\sum_{12}$PAHs (µg.kg^{-1} dw)**	**$\sum_{28}$PCBs (µg.kg^{-1} dw)**
STP1	1839.8	301.9
STP2	720.8	91.4
STP3	1146.1	57.3
STP4	1387.9	26.5
STP5	825.8	17.9
STP6	2116.7	49.5
STP7	383.8	20.9
STP8	375.3	26.8
STP9	532.8	45.8
STP10	493.8	53.2
STP11	578.4	29.8
STP12	180.3	21.6
STP13	194.0	32.4
STP14	348.3	19.6
STP15	328.7	30.7
TEL – PEL	**655-6676**	**22-189**
ERL – ERM	**4022-44792**	**23-180**

The present paper is the first study on the evaluation of organic contamination level in Tripoli harbour. Our work provides a data base about two classes of persistent organic pollutants

(PCBs, PAHs and Me-PAHs) in sediments collected from 15 stations of Tripoli harbour Basins. Multiple sources can be associated to PAHs and PCBs pollution into the harbour basin. However, the diagnostic ratios indicate that pyrogenic process is the dominance source. It is characterized by the abundance of high molecular weight of PAHs resulting from coal dust and the combustion of biomass and coal. However, the minor contribution of petroleum product produced by shipping activities, accidents oil spills and leakage from boats and ships, sewage outfall and fishery activities is due to the vulnerability of petroleum PAHs for degradation. Moreover, petroleum PAHs are characterized by low molecular weight PAHs that are more soluble in water. In order to determine the coefficient distribution between sediment and water, become necessary to quantify PAHs in water samples in Tripoli basins. The evaluation of ecotoxicological risk based on SQGs of PAHs suggests that the biological adverse effects are expected occasionally for fishery basin and old basin of harbour. In addition, the concentration of total PAHs in Tripoli basins varied between 243 and 2965 µg.kg^{-1} dw, could be considered as moderate to high polluted with PAHs according to Baumard et al. (1998) classification. Concerning the PCBs contamination, the biological adverse effects are expected occasionally for the overall of Tripoli Port basins. Based on these results, it is now urgent to adopt adequate pollution control strategies particularly in this harbour basins where the remobilization of these organic pollutants occurred frequently from sediments due to dredged activities and the continued development of Port activities which lead to intensive maritime transport into Tripoli harbour.

Acknowledgements

This work was financially supported by WILDCAT COMPANY and Tripoli Harbour Authority and the Laboratory of Marine and Analytical Chemistry of Lille1 University. The authors would like to thank Dr David Dumoulin for all the technical support and assistance in the GC-MS analysis.

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Article 2

ASSESSMENT OF PERSISTANT ORGANIC POLLUTANTS IN SURFICIAL SEDIMENTS ALONG LEBANESE COASTAL ZONE

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Submitted Paper

Date

00/00/2015

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Abstract

15 surficial sediments was collected from five hotspots stations influenced by various industrial units, freshwater input and touristic activities in particular at semi-closed basins including (eg., Abou Ali estuay, Chekka and Jounieh Bay, Port of Beirut and Port of Jiyeh power plant) to assess POPs (16 PAHs, 18 Me-PAHs and 28 PCBs) contamination along Lebanese Costal Zone (LCZ). Total mean of individual concentrations of PAHs (∑16PAHs) are ranged between 537.1 and 3772.6 µg.kg^{-1} dw, with an average concentration of 1035.4 µg.kg^{-1} dw, $\sum_{18}$Me-PAHs are ranged between 187.2 and 11541.1 µg.kg^{-1} dw with an average concentration of 2617.2 µg.kg^{-1} dw and $\sum_{28}$PCBs were ranging from 142.6 to 1303 µg.kg^{-1} dw with an average concentration of 550.8 µg.kg^{-1} dw for all stations. Significant contamination was localized at Beirut Port surrounded by densely populated area and subjected to multidisciplinary activities with intensive sedimentation and limited water circulation. The composition profile show the abundance of PAHs with MMW and HMW at Abou Ali estuary, Chekka Bay and Beirut Port Beirut sediments where the pyrogenic processes are the predominance source while PAHs with LMW are greater represented at Jounieh Bay and Jiyeh power plant where the petrogenic processes are the major sources of pollution with PAHs. Source identification of PAHs was confirmed using LMW/HMW diagnostic ratio. For PCBs, LCZ is polluted by higher chlorinated congeners with 4 to 9 chlorinated atoms. An interpretive analysis of literature results and composition profile of PCBs congeners suggesting that atmospheric deposition is a primarily source of PCBs emissions. Toxicity and biological risk were assessed using toxic equivalent quantity (TEQcarc) and sediment quality guideline quotient (SQGq). The potential biological adverse effect of PAHs and PCBs on aquatic ecosystems were expected ranged from low to medium - low according to SQGq.

Keywords: POPs, Sediments, LCZ and SQGq.

Introduction

It’s our coast, let’s defend to protect it…Be ready for the change…It’s not too late!

Coastal zones throughout the world are attractive areas for human settlements due to economic development and opportunities. It is estimated that 50% of the world’s population inhabit coastal zones on approximately 10% of the earth’s surface. In Lebanon, over 75% of the population and economic activity are concentrated in this zone, which is attributed to the centralized nature of the economic and political systems in the country (UNDP, 1992; Shi et al., 2001). In addition, the Lebanese civil war which lasted 15 years from 1975 to 1990, was imposed a huge pressure on the biophysical environment of Lebanese coastal zone (LCZ). This area suffered extensive infrastructure damage and internal displacement of almost one million people (Republic of Lebanon, 1997, 2001; Global IDP database, 2004). Further pressure on the biophysical environment of coastal regions will impose proportionally to this trend of population concentration in coastal areas which is expected to continue into the future (El Sabh et al. 1998). Given this rapid rate of development, LCZ is suffering also from uncontrolled urban sprawl and unplanned development (El Asmar et al., 2014). 2.5 million Lebanese living on coastal produce 950000 m^3 of wastewater, which discharged directly into the sea (CDR/ECODIT-IAURIF, 1997; Green Peace, 2007; UNEP, 2007). Our situation was further compounded by the Israeli invasion. One of the most high profile issues of the conflict was the bombing by Israeli air raids of the Jiyeh power plant south of Lebanon between 13 and 15th July 2006, which resulted in the spillage of thousands of tons of oil into the Mediterranean Sea. 150 km long, which represents two thirds of the Lebanese coastline, was contaminated (Green Peace, 2007; UNEP, 2007; Maslo et al., 2014). On December 2006, the International community considered through the General Assembly Resolution 61/194, that “the oil slick has heavily polluted the shores of Lebanon and consequently has serious impact on human health, biodiversity, fisheries and tourism” (Green Peace, 2007). The Lebanon oil spill event is one of the biggest environmental catastrophes in the Eastern Mediterranean Sea and was the most visible environmental impact of the war, resulting in both short and long term threats to the coastal marine environment of Mediterranean Sea (Green Peace, 2007). The European Environment Agency (EEA) 2006 showed that the Arab Mediterranean coastline suffers from common major threats as untreated sewage discharges, intensive coastal development, oil and chemical pollution from industrial sites as well as a lack of solid waste management (PNUE/AEE 2006). Lebanon is a typical case of most coastal areas of the developing countries in the region. A wide range of anthropogenic activities are contributing to water pollution of LCZ and overall environmental degradation. The intensive coastal urbanization involves the concentration of industrial activity along the coast and therefore, increases the release of untreated chemical waste into sea leading to a particular threat to marine ecosystem (Green Peace, 2007). Serious negative health impacts could be inevitable (El Asmar et al., 2014).

Urban and industrial discharges are potential sources of organic pollutants including the polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). PAHs and PCBs are widespread and ubiquitous contaminants in marine environment (La Flamme and Hites, 1978; Gschwend and Hites, 1981; NOAA, 1988; Jonsson et al., 2003; Lohmann et al., 2007; Huang et al., 2012) and may be most commonly associated with oil spills and/or domestic and industrial discharges (King and Chou, 2003). Coastal sediments are one of the major sinks of the mixtures of these persistent organic pollutants (POPs) with levels higher 1000 times than water column concentrations (Luca et al., 2005), causing a serious problems due to their toxicity, persistence to biodegradation and their ability to accumulate in the biota up the food chain (Peachey, 2003; Guzzella et al., 2005; Qiu et al., 2007; Morillo et al., 2008; Wade et al., 2008; Huang et al., 2012). In the other hand, sediment resuspension has been identified as a key process capable of reintroducing POPs to the water column (Jurado et al., 2007; Lohmann et al., 2007). Therefore, due to its ecological importance, the evaluation of coastal sediment quality constitutes an important area of research (Silva et al., 2004; Usero et al., 2008). Moreover, limited water exchange makes the Mediterranean Sea very sensitive to the build-up these pollutants (Green Peace, 2007). Therefore, amongst the numerous environmental concerns we are facing, the marine environment is one of the top priorities that must be addressed. Environmental protection is well covered in national and international agreements and conventions both generally and in the specific case of war time (Takshe et al., 2010). Lebanon is a party of many conventions was established to protect the Mediterranean Sea against pollution. Barcelona Convention addresses the protection of specially protected areas and biodiversity in the Mediterranean Sea through the elimination of pollution from land-based sources and the establishment of marine protected areas (MAP 2005; Green Peace 2007). The Convention for Biological Diversity (CBD) urges Parties and other Governments to make efforts to adopt a marine and coastal management framework for marine and coastal protected areas (COP 7, 2004; CBD, 2007; Green Peace 2007). And, MARPOL 73/78 Convention (Annex 1 Regulation 10) defined Mediterranean Sea as a “Special Sea Area”, where the discharge of oil or oily mixtures from ships is entirely prohibited with only minor and well defined exceptions. Unfortunately, there is no monitoring infrastructure of such practices in Lebanon. Indeed, Lebanon is undergoing an exciting period of urban transformation which has manifested it in huge commercial, residential, and industrial property development. A casual observation reveals that these physical developments adhere to no sustainable patterns of development exemplified by water pollution which become the defining characteristics of Lebanon’s coastal areas.

LCZ is a narrow and discontinuous strip formed of river-deposited alluvium and marine sediments, which alternate with rocky beaches and sandy bays and extends over 220 km along the Eastern Mediterranean Sea (Zahreddine et al., 2004; Grean Peace, 2007; UNEP, 2007).

The coastal area of Lebanon is exposed to a number of chronic anthropogenic stress factors (e.g. the release of untreated sewage and industrial effluent) (UNEP, 2007). In Beirut area and to the north, numerous cities and towns dot the narrow coastal strip and do not have wastewater treatment systems. Untreated domestic and industrial wastewaters are discharged into the Mediterranean along the length of the coast, leading to high levels of organic pollutants and human pathogens in many locations (UNEP, 2007). We found over 53 network pipelines of wastewater on the coast of Lebanon including Ports areas (MoE, 2001; Green Peace, 2007). However, the untreated sewage waste and solid waste dumping are not the only polluting threats to the Lebanese coastline (Green Peace, 2007). The general deterioration of the coast and the increasing pressure on marine habitats and coastal ecosystems are due to the combined effects of concentrated residential, industrial, and tourism development, infrastructure and construction activities. Indeed, several industrial plants are located on LCZ which hosts four commercial ports and over 15 fishing harbors, dozens of sea pipelines for petroleum imports, three fuel power plants and series of various industries and factories (El Asmar et al., 2014). In addition to coastal point sources, inland activities contribute the pollutants into the Mediterranean by drainage along the rivers. From a dynamic point of view, semi-enclosed basins such as Ports and estuaries where occurred chronic pollution from shipping and other industrial activities requires more detailed fingerprinting of different contaminant sources (Zahreddine et al., 2004). In this study we have investigates the contamination level of emerging POPs, in particular 16 PAHs, 18 Me-PAHs and 28 PCBs in 15 superficial coastal sediment samples collected from five potential hotspots zones of pollution along the Lebanese coastline in order to identify their main released sources and thus their potential toxicological effects by comparison with sediment quality guidelines levels (SQGs). The study provided a first baseline data help to improve our understanding about the status of the Lebanese coastal ecosystem and stimulate policy makers for achieving an integrated coastal zone management (ICZM).

Materials and Methods

Sampling stations

Lebanese coast are being destroyed and replaced with beach resorts, large commercial facilities, industrial units and harbors (Zahreddine et al., 2004). This intensive anthropogenic activity is a potential source of coast pollution. Wherefore, the sampling stations were selected to cover LCZ with various industries and estuaries, particularly that influenced by intense shipping, freshwater input and touristic activities closed to several hotspots adjacent to the Lebanese coastline; which represent a wide range of environmental conditions in particular at ports and bays where the remobilization of coastal sediment has been identified as a key process capable of reintroducing contaminants like POPs to the water column which pose a potential risk to the wildlife ecosystem and human health (Jurado et al., 2007; Lohmann et al., 2007; Huang et al., 2011).

In fact, our study is the first since no investigations have been carried out on the organic contamination along LCZ. However, this assessment covers about 110 km of Lebanese coastline extending from Jiyeh to Tripoli city (Eastern Mediterranean Sea, Lebanon) (Fig.19). Fifteen surficial sediment samples was collected from five sampling stations including; the commercial Port of Beirut, the Port of Jieh Power Plant, Abou Ali estuary, Touristic beach in Chekka bay, and Touristic beach in Jounieh bay (Fig.19). The GPS coordinates and other characteristics of the studied sites are presented in Table 10.

Fig. 19: Lebanon map shows the location of five selected sampling stations along LCZ.

Table 10: Description of the five investigated sampling sites along LCZ.

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

Port of Beirut is the main important harbor in Lebanon and is one of the largest and busiest ports on Mediterranean Sea due to its role in the maritime trade between East and West. It is located in the center of Lebanon and has been serving Capital of Beirut for shipping, transportation and fishery activities for the past several hundred years, the harbor covers an area of approximately 1,2 km^2.

Jiyeh power plant is located in Jiyeh city directly on the coastline at 30 kilometers south of Beirut . It's total area comprises some 40,000 m². The harbor activities is essentially reserved for petroleum products where the fuel supply to this power plant will continue to be by ship from the Mediterranean Sea.

Chekka Bay, the samples was collected from private beach resort located in Chekka costal city situated 65 km north of Beirut. This is affected by touristic activities and the presence of yachting center. Furthermore, the different levels and orientation of industrialization development in this area due to the presence of multiple industries in particular two cement factories located about a hundred meters away from this beach provide an interesting contrast for understanding pollutants source and distribution mechanisms in this marine ecosystem for our knowledge of the potential risk and actual danger to the human health. We should to note that the samples were collected from this beach due to the difficulties to access to the basins of these factories. In the other hand, from Jounieh Bay, the samples were collected from private beach also located in Jounieh costal city about 17.8 km north of the Beirut. This beach located on this natural bay host this city for touristic activities without the presence of any significant influence by industrial activities like the case of Chekka bay.

Abou Ali River in north Lebanon extends of 44.5 km long and its basin encompasses nearly 236 towns and villages where live around 800,000 inhabitants. The source is at an elevation of 1850 m and the river falls to nearly sea level passing through Tripoli coastal plain, the second largest Lebanese city with approximately 350,000 inhabitants making it highly affected by anthropogenic activities. The Abou Ali River catchment basin area is estimated at 484 km^2 of which 97 percent is mountainous with average flow rates in dry season (October) and wet season (March) are approximately 0.8 $m^3 s^{-1}$ and 17.2 $m^3 s^{-1}$, respectively (Massoud et al., 2006). The Tripoli coastal area receives approximately 369 Mm^3/year freshwater inputs from Abou Ali River (Kabbara et al., 2008), where the samples was collected from the estuary of this river on the Mediterranean Sea.

Sampling and analysis strategy

In May 2014, fifteen superficial sediments samples (top 5 - 10 cm) were collected from five stations along LCZ (Fig.19). Each sample was homogenized before being transferred into pre-calcinated aluminum containers capped with aluminum foils. Three surface sediment samples were collected for each station at different depth below water surface. Sediment samples were transported in the laboratory and dried at room temperature in a laminar hood.

Sediments samples were analysed for 16 PAHs, 18 Me-PAHs and 28 PCBs including 12 dioxin-like PCBs (PCB-DL) and the 7 indicators PCB (PCBi). The extraction, purification, and instrumental analysis for PAHs, Me-PAHs and PCBs quantification have been carried out according to the procedure reported by Net et al. (2014) and Merhaby et al. (2015). Final extracts were analyzed by using a Varian 3900 gas chromatograph (GC) equipped with a deactivated fused-silica guard column (5 m, 0.53 mm i.d.) and a fused-silica capillary

Phenomenex XLB (60 m length, 0.25 mm i.d., 0.25 µm film thickness) and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS). The GC-MS conditions have been reported by Merhaby et al. (2015) and Rabodonirina et al. (2015).

Quality assurance and quality control (QA/QC) of the data

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

Results and Discussion

PAHs, Me-PAHs and PCBs concentrations

The mean concentration of each targeted compounds and the sum of 16 PAHs ($\sum_{16}$PAHs), 18 Me-PAHs ($\sum_{18}$Me-PAHs) and 28 PCBs ($\sum_{28}$PCBs) for each station are summarized in Table 11. The highest concentration of $\sum_{16}$PAHs was found at Port of Beirut (3772.6 µg.kg^{-1} dw) followed by Jounieh Bay (997.1 µg.kg^{-1} dw), Abou Ali estuary (667.8 µg.kg^{-1} dw), Port of Jiyeh Power Plant (552.4 µg.kg^{-1} dw) and the minimum was determined at Chekka Bay (537.1 µg.kg^{-}

^{1} dw) (Fig. 20A). High level of PAHs in Port of Beirut may be due to the multiple activities in this harbour. Indeed, loading and unloading operations, shipping, transportation, fishery activities, industrial effluents, ships and urban discharges are mainly the sources of PAHs contamination and these activities are intense in Port of Beirut. While the $\sum_{16}$PAHs in Chekka Bay was the lowest and seven times lower than $\sum_{16}$PAHs found in Port of Beirut. Chekka Bay is a touristic resort port and influences only by touristic activities. Therefore, this lowest concentration can be explained due to the physico-chemical properties of these pollutants, which dedicate their environmental behavior (Wania, 2003, 2006; Lohmann et al., 2007). According to Baumard et al., (1998a), the classification of PAHs pollution levels assigned as: low 0-100 ng/g; moderate >100-1,100 ng/g; high > 1,100-5,000 ng/g; and very high > 5,000 ng/g. Based on this classification, we suggest that it could be considered as moderate for all sampling sites except for Port of Beirut which is highly polluted with PAHs.

Concerning the $\sum_{18}$Me-PAHs along LCZ, the average was determined at 2617.2 μg.kg^{-1} dw with the range of 187.2-11541.1 μg.kg^{-1} dw. The highest concentration of $\sum_{18}$Me-PAHs was detected at Port of Beirut (11541.1 μg.kg^{-1} dw) followed by Port of Jiyeh Power Plant (731.2 μg.kg^{-1} dw) (Fig. 20A). High level of Me-PAHs in Beirut Harbor may due to chronic exposure originated from ship discharges and ships maintenance, oil spills accidents, oil leakage during oil supply for fishery boats and harbor effluents (Lamparelli et al., 1993). Whilst lowest $\sum_{18}$Me-PAHs (187.2 μg.kg^{-1} dw) was found at Jounieh bay for sediments collected from a touristic resort port.

For PCBs, the $\sum_{28}$PCBs is presented in Figure 20a. 24 PCBs congeners (PCBs 28, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 167, 169, 170, 180, 187, 189, 195, 206, and 209) were quantified for each superficial sediments samples collected from five sampling stations along LCZ. The $\sum_{28}$PCBs were ranging from 143 (Jounieh Bay) to 1303 μg.kg^{-1} dw (Port of Beirut) with an average of 505.8 μg.kg^{-1} dw. High level $\sum_{28}$PCBs in Port of Beirut might be due to the emission of PCBs from paints, old equipment or materials used in some vessels call the harbor particularly during the activities of ships maintenance (shipyard) and might be associated with the use of capacitors and transformers in the industrial area into this harbor and industrial activities surrounded. Indeed, PCBs can be originated from shipping and industrial activities (Bícego et al., 2006; Hong et al., 2005, 2006). Similar results were reported for the Korean coastal areas (Duan et al., 2013). Hence, we suggest that the shipping and industrial activities with low local hydrodynamics as possible sources of the PCBs accumulation in the sediments at Port of Beirut basin. The lowest concentration of $\sum_{28}$PCBs was determined at Jounieh Bay where influenced only by the touristic and fishing activities. For the Port of Jiyeh power plant and Chekka Bay, the $\sum_{28}$PCBs were detected respectively at 718.2 and 250.6 μg.kg^{-1} dw.

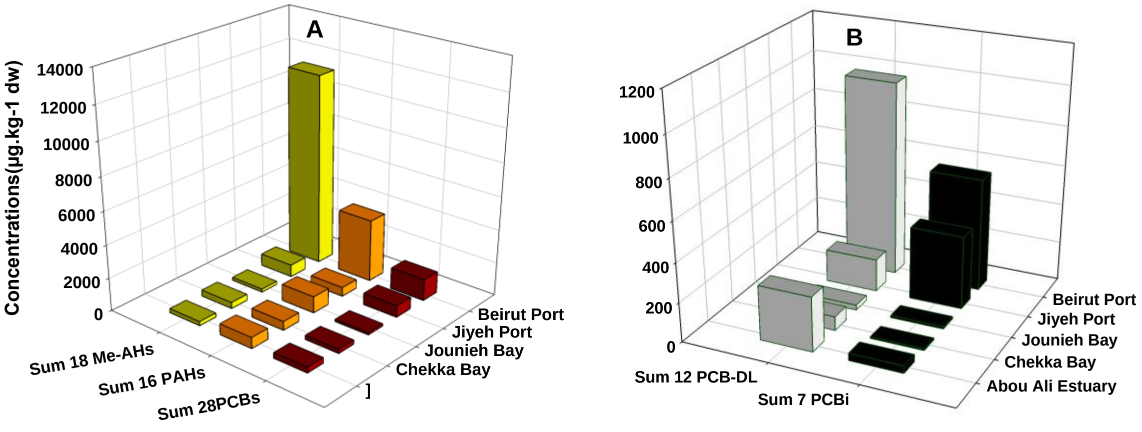

Fig. 20: **(A)** Σ16PAHs, Σ18Me-PAHs, Σ28PCBs and **(B)** percentages Σ7PCBi and Σ12PCB-DL of Σ28PCBs for the five sampling stations selected along LCZ.

Among these 28 PCBs, 7 PCBs (CB 28, 52, 101, 118, 138, 153 and 180) were known as PCBs indicators ($\sum_{7}$PCBi) due to the most abundant in the environment and 12 congeners (CB 77, 81, 105, 114,118, 123, 126, 156, 157, 167, 169, and 189) were called PCBs dioxin-like (Σ12PCB-DL) due to their high toxicity, persistency in the environment and their potential health effects (Kimbrough et al., 2010; Tanabe and Minh, 2010). Indirect PCBs exposure from environment can cause neurobehavioral effects and development in children (Jacobson and Jacobson, 1996; Korrick, 2001), memory and learning impairment in older adults (Schantz et al., 2001), endocrine mediated effects including shortened menstrual cycle (Mendola et al., 1997), and other nonspecific reproductive effects (Ross. 2004). While, direct occupational or accidental exposures can cause chloracne and other effects related to chronic dermal and ocular irritation (James et al., 1993). In this study, the $\sum_{7}$PCBi were found in the range of 7.9 - 574.8 µg.kg^{-1} dw and the Σ_{12}PCB-DL were found in the range of 25.8 – 988.8 µg.kg^{-1} dw. Figure 20B shows the concentrations of $\sum_{7}$PCBi and Σ_{12}PCB-DL for the five sampling stations selected along LCZ. The percentages of Σ_{7}PCBi represented 3.15 %, 7.67 %, 10.97 %, 44.11 % and 51.91 % at Chekka Bay followed by Jounieh Bay, Abou Ali estuary, Port of Beirut and Port of Jiyeh respectively, while for Σ_{12}PCB-DL represents 18.09 %, 23.15 %, 28.12%, 75.88 % and 81.59 % at Jounieh Bay, Port of Jiyeh power plant, Chekka Bay, Port of Beirut and Abou Ali estuary respectively. The highest concentrations for both Σ_{7}PCBi and Σ_{12}PCB-DL were observed at Port of Beirut with 574.8 and 988.8 µg.kg^{-1} dw respectively (Fig. 20B). The Σ_{12}PCB-DL which are the highly toxic congeners were dominated for all the stations except for Port of Jiyeh power plant (Fig. 20B). Beside the harbour activities which lead to a large amount of PCB-DL in sediments, Abou Ali estuary shows also an important amount of PCBs and PCB-DL represent 81.59 % which indicate that this river is highly affected by anthropogenic activities

(Massoud et al., 2006). In fact, Abou Ali River flows through an urbanized region with high-density population (Tripoli City). Many industries comprise small facilities scattered throughout the river including car repair workshops, food processing establishments, furniture manufacturing and woodcrafts, restaurants, various shops (CES, 2001) and three hydroelectric plants along the river with a combined nominal capacity of 12.1 MW (SOER, 2001). Plus, the Northern coastal area of the river mouth is targeted to become the industrial zone of the Tripoli district where a major wastewater treatment plant which still not operated at present in full capacity of 40,000 m^3 and various industrial units was constructed in the same area (JICA and CDR, 2001). Therefore, the combination of different pollution sources including solid waste dumping sites in open area 65,000 m^2 located on the coast near the mouth of Abou Ali River (CES, 2001), the dumping of wastes, discharging of waste water and industrial effluent directly to the river with the average annual rate is 262 million m^3 (SOER, 2001; Doong et al., 2008) lead to this organic contamination by these highly toxic congeners in the estuary (Greenpeace, 2007; Kabbaraa et al., 2008). Abou Ali River acts as transit zones where the contaminants are transported from rivers to the sea (Oros and Ross, 2004; Wang et al., 2008). In this study, we observed that Σ_{12}PCB-DL are the most frequently detected in our sampling stations along LCZ.

The highest content of PAHs, Me-PAHs and PCBs was detected at Port of Beirut. This contamination may be due to both the urban and industrial activities and the intensive sedimentation (Konat and Kowalewska, 2001). Indeed, Port of Beirut has the limited water circulation and low exchange with the open sea, the closed basins mainly is responsible for this localized pollution in comparison with other stations (Luca et al., 2004; Bícego et al., 2006). Port of Beirut was contaminated by PAHs, Me-PAHs and PCBs higher than which determined in Tripoli harbor reported by Merhaby et al. (2015). However, the concentrations of PAHs, Me-PAHs and PCBs in surface sediments show a random distribution between surface samples collected at different depth below water column at each station. The contamination level increase with the increase of depth at SCB, SPB and SAE stations for PAHs, Me-PAHs and PCBs respectively (table 11). Wherefore, we can suggest that this random distribution mainly influenced by multiple factors including potential sources, sorbing phases, geological composition of sediments (mainly consist of sandy clay), meteorological conditions (precipitation patterns, wind speed, temperature), circulation patterns (currents and wind waves), sedimentation process, hydrodynamic transportation and surrounding food web structure, (Guo et al., 2003; Lohmann et al., 2007).

Table 11: List of targeted compounds and mean of Individual concentration of PCBs, PAHs and Me-PAHs in µg.kg^{-1} dw for sediment samples collected from five sample stations along LCZ (mean of three determinations) with the total mean values at each station.

16 PAHs

Compounds	**Abou Ali stuary**	**Chekka Bay**	**Jounieh Bay**	**Port of Beirut**	**Port of Jiyeh**
Nap	11.9	12.9	231.8	225.6	72.9
Acy	3.1	2.8	0.9	36.7	50.2
Ace	10.9	3.9	13.1	40.7	54.5
Fl	5.9	42.4	11.5	48.9	39.3
Phe	43.1	56.3	334.5	65.9	79.9
Ant	8.1	2.7	141.2	169.3	71.3
Pyr	22.6	13.9	11.3	59.9	2.3
Flu	35.4	19.2	8.5	390.9	32.0
BaA	12.1	1.4	ND	519.3	17.8
Chr	13.4	3.9	2.3	165.4	20.2
BbF	60.9	38.2	24.6	466.7	7.8
BkF	118.9	70.8	91.7	302.5	39.3
BaP	69.5	34.1	47.4	358.1	10.6
IP	98.4	80.8	78.2	161.6	29.5
DBA	86.6	45.3	ND	396.3	ND
BgP	67.0	108.7	ND	364.7	24.7
$\sum_{16}$ *HAPs*	667.8	537.1	997.1	3772.6	552.4
18 Me-PAHs					
1-methylnaphthalene	7.1	35.1	14.5	130.9	19.3
2-methylnaphthalene	7.8	45.5	15.1	72.8	24.3
1,2-dimethylnaphthalene	15.1	107.2	36.2	306.0	67.4
1,6-dimethylnaphthalene	13.0	77.8	31.4	232.9	52.9
2,6-dimethylnaphthalene	12.2	57.9	59.9	121.7	58.3
1-methylphenanthrene	8.1	3.9	0.9	648.6	11.6
2-methylphenanthrene	10.6	3.3	1.1	1164.9	14.4
3-methylphenanthrene	8.2	3.4	1.3	3913.1	44.5
9-methylphenanthrene	12.7	3.1	0.9	1339.8	51.3
2-methylanthracene	10.2	2.6	0.8	714.5	16.3
1,7-dimethylphenanthrene	22.1	8.2	3.1	1999.4	77.8
Retene	31.7	10.8	7.4	ND	41.6
1-methylfluoranthene	15.5	2.9	1.8	116.2	10.0
3-methylfluoranthene	14.7	3.5	1.9	148.4	9.9
1-methylpyrene	13.6	2.4	1.7	207.7	77.5
4-methylpyrene	9.2	3.6	1.8	215.5	62.4
3-methylchrysene	20.2	1.6	3.4	ND	44.1
6-methylchrysene	18.9	2.9	3.9	208.6	47.7
$\sum_{18}$ *Me-PAHs*	250.8	375.7	187.2	11541.1	731.2

28 PCBs

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

* ND: not detected and indicates 0 µg.kg^{-1} dw.

Composition and source identification of PAHs and PCBs

The majority of PAHs were detected and quantified in all samples except for sediments collected from Jounieh Bay were the concentrations of PAHs with 6-rings was unquantified. However, the PAHs composition profile shows the dominance of high molecular weight PAHs (HMW-PAHs) with 5-rings (BbF, BkF, BaP, IP) and 6-rings (DahA and BghiP) with percentage values reached 52.08 % and 22.99 % for samples collected from Abou Ali Estuary and 41.68 % and 28.67 % for samples collected from Chekka Bay, respectively (Fig. 21A). At Beirut Port, the dominance was determined for medium molecular weight PAHs (MMW-PAHs) with 4-rings (Pyr, Fluo, BaA, Chry) and high molecular weight (HMW-PAHs) with 5-rings (BbF, BkF, BaP, IP) which accounted for 30.10 % and 34.16 % respectively. For Jounieh Bay and Jiyeh Port, the results show the dominance of low molecular weight PAHs (LMW-PAHs) with 3-rings (Acy, Acn, Flu, Phe and Anth) with percentage values reached 50.27 % and 53.45 % respectively (Fig. 21A). PAHs with MMW and HMW are the most abundant at Abou Ali estuary, Chekka Bay and Beirut Port. In contrast, PAHs with LMW are dominant at Jounieh Bay and Jiyeh power plant. High levels of four- and five-rings hydrocarbons are distinctive of mixtures formed by the combustion of fossil fuels (Gogou et al., 2000). However, this wide range of PAHs composition profile compounds with different percentages at each station (Fig. 21A) indicates that there are potentially multiple sources of PAHs contamination in each station, mainly related to harbour, touristic and fishery activities occurred including shipyards, ships or boat discharges, anchoring area, loading/unloading operations, accidental oil spills, industrial effluents, and sewage outfalls and/or may be transported via river such as the case of Abou Ali estuary and atmospheric input (Zhou and Maskaoui, 2003). However, LMW are more volatile and degradable in the environment (Quantin et al., 2005; Merhaby et al., 2015) than HMW so their abundance at Jounieh Bay and Port of Jiyeh power plant indicate the presence of continuous input sources at these stations. Although, It is interesting to note that LMH-PAHs (two- and three-rings) are produced from petroleum products, fossil fuels and biomass incomplete combustion at low to moderate temperature and natural digenesis, while MMW and HMW-PAHs (four- or more rings structures) are produced at high temperature (Yuan et al., 2001; Mai et al., 2002). Hence, each PAH has a proper potential hazardous effects; PAHs with four- to seven-rings are highly mutagenic and PAHs with two- or three-rings are highly toxic (Fernandes et al., 1997; Law et al., 1997; Zhou and Maskaoui, 2003; Nakata et al., 2003).

For Me-PAHs, the results show that Me-PAHs with 3-rings were observed in majority for samples collected from Abou Ali estuary and Port of Beirut which account for 41.26 % and 84.74 % respectively. However, Chekka Bay and Jounieh Bay were dominance by 2-rings Me-PAHs, which reached 86.10 % and 83.95 % respectively (Fig. 21B). No significant variation was observed concerning the composition of Me-PAHs with 2, 3 and 4-rings for samples collected from Jiyeh Port; their values were determined 30.39 %, 35.21 % and 34.40 %

respectively (Fig. 21B). It is interesting to note that substituted Alkyl PAHs (Me-PAHs) is a tracer of petroleum input confirming the presence of oil residues from multiples sources at all investigated stations mainly due to shipping activities, accidents oil spills and leakage from boats, yachts and ships, sewage outfall, fishery activities and river input.

The concentration percentages of low chlorinated PCBs congeners (1-3 chlorines), medium (4-6 chlorines) and high chlorinated congeners (7-10 chlorines) of all sampling stations are presented in Fig. 21C. There is no specific dominance for the distribution of PCBs. The composition of PCBs was dominated by the content of 7 Cl CB (69.15 %) at Abou Ali estuary, 9 Cl CB (41.22 %) at Chekka Bay, 8 and 9 Cl CB (34.75 and 39.35 %) at Jounieh Bay, 5 Cl CB (56.06 %) at Port of Beirut and 4 and 6 Cl CB (30.03 and 34.21 %) at Port of Jiyeh power plant (Fig. 21C). Whereas, only small amount of congeners with 2-3 Chlorine atoms (<4.65 %) accumulated into the sediments. Above all, LCZ was polluted by higher chlorinated congeners characterized by the abundance of Medium to High chlorinated PCBs (4-9 Chlorine atoms). In addition, the occurrence of a wide range of chlorinated congeners at our sampling stations suggesting the use of a variety of commercial mixtures thus indicating a strong relation between the composition pattern/concentration of PCBs in environment matrices and anthropogenic pollution (Bícego et al., 2006; Duan et al., 2013). However, the dominance of higher chlorinated congeners at all sampling stations can be explained based on several environmental processes. Indeed, two major processes may affect the fate and composition of PCBs in water are dissolution and anaerobic dechlorination causing opposite trends in homolog distribution pattern (low, medium and high Cl CBs). The anaerobic dechlorination process is characterized by a decrease in higher chlorinated congeners with the increase in lower congeners as a result of microbial dehalorespiration (Li et al., 2009). In water, these low congeners tend to be more susceptible to the dissolution loss process (Li et al., 2009). In atmosphere, due to their high solubility and volatility, lower chlorinated PCBs can be degraded easily by hydroxyl radicals (Mandalakis et al., 2003), whilst the higher chlorinated congeners are more persistent in the environment (Ross. 2004). Moreover, a supplementary phenomenon was reported by Hornbuckle et al. (2004), suggesting that PCBs tend to be higher when sediment resuspension event was more important induces a vertical fractionation of PCBs congeners leading to the loss of lower chlorinated PCBs compared with higher ones (Li et al., 2009). Based on our results, we can suggest that the dissolution process may affect significantly the PCBs distribution and composition pattern at all studied stations along LCZ leading in consequence to a potential risk for wildlife and human health based on the possibility that these congeners are absorbed by mussels and fishes (Ross. 2004). Recent studies have shown that each PCBs congener has different biological activity and toxicity due to the number and position of chlorine atoms in the structure. In addition to toxic effect exert by PCBs-DL mentioned previously; also, neurotoxic effects have been observed for the ortho-substituted congeners, with two or more ortho-chlorines (Schantz, 1996; Rice and Hayward. 1997). Although, these different processes controlling PCBs behaviour in the environment, large amount of high chlorinate PCBs at Beirut Port indicates that these contaminants are unintentionally released from human activities thus transported primarily through atmospheric processes including wetfall, dryfall and river inputs and water-air exchange (Strachan and Eisenreich, 1990; Li et al., 2009).

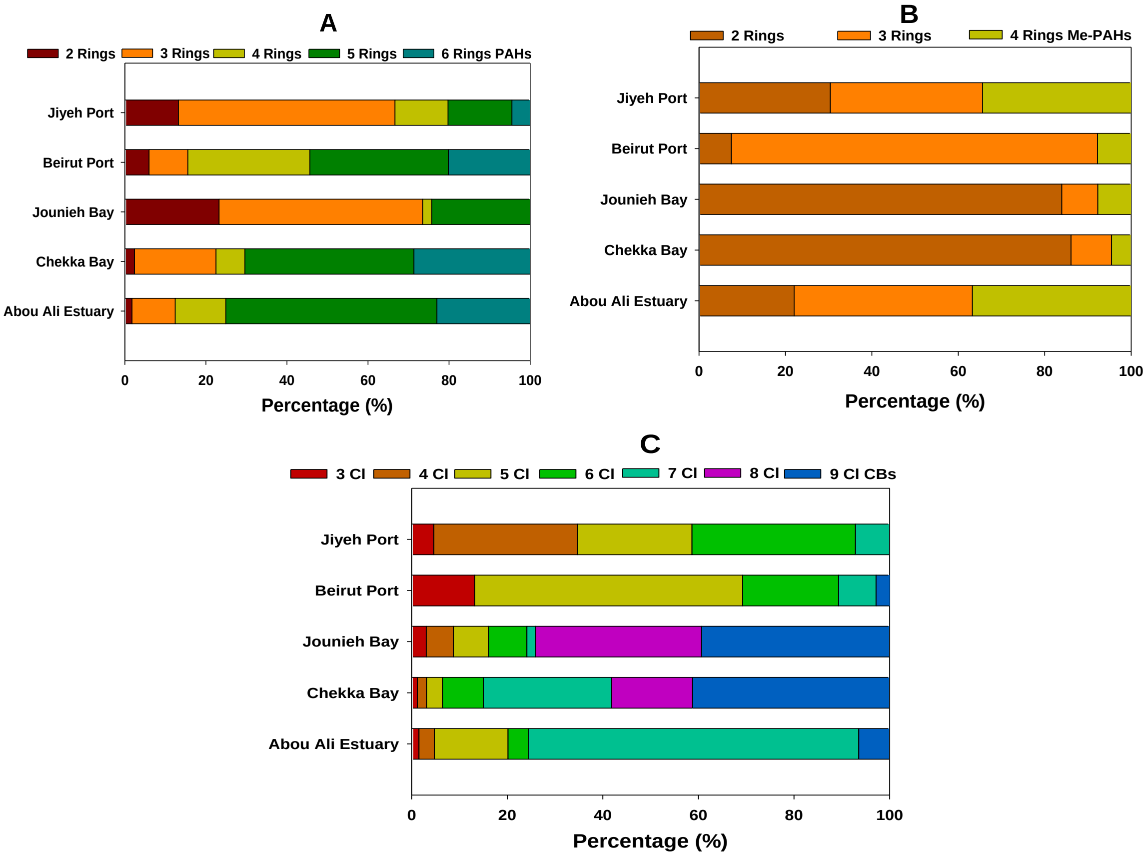

Fig. 21: Composition profile pattern for **(A)** PAHs, **(B)** Me-PAHs and **(C)** PCBs in samples collected from five sampling stations along LCZ.

Sources of anthropogenic PAHs in coastal marine sediments belong to two processes: petrogenic and pyrogenic, based upon the predominance of different PAHs congeners. This mean that pyrogenic sources include both high and low temperature combustion processes (e.g., fossil fuel combustion, forest fires, shrub and grass fires) characterized by abundance of HMW PAHs (Wang et al., 1999), while petrogenic sources is closely related to the direct release of crude and refined petroleum products (e.g., oil spills, power plant, oil pipes, urban runoff, oil seeps and road construction materials) (Luca et al., 2004) characterized by abundance of LMW-PAHs and alkylated PAHs (Simpson et al., 1996; Fernandes et al., 1997; Zhou et al., 1998; Barakat et al., 2011). Therefore, several molecular and isomeric pairs ratios of PAHs have been used in order to survey their sources. The origin of surficial sediments along LCZ is summarized in Table 12: (A) Characteristic values and (B) source identification based on selected molecular, isomeric and homologue alkyl PAHs ratios for petrogenic and pyrogenic origins of PAHs for sediment samples collected from five sampling stations along LCZ. (Baumard et al., 1998; Budzinski et al., 1997; Yunker et al., 2002).

Table 12: **(A)** Characteristic values and **(B)** source identification based on selected molecular, isomeric and homologue alkyl PAHs ratios for petrogenic and pyrogenic origins of PAHs for sediment samples collected from five sampling stations along LCZ.

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

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

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

The use of molecular ratio Flu/Pyr (Budzinski et al., 1997; Magi et al., 2002) only could prevent a misleading diagnostic of PAH sources according to what suggested by Raoux (1991), and Baumard et al. (1998a). The ratio Flu/Pyr <1 indicates petrogenic inputs while ratio Flu/Pyr ratio >1 indicates pyrogenic sources (Sicre et al., 1987; Baumard et al., 1998b; Magi et al., 2002). Furthermore, isomeric pairs ratios such as BaA/228 or BaA/ (BaA+Ch) and IP/276 or IP/IP+BghiP are also frequently used in the identification of PAHs sources in environmental samples. BaA/228 <0.20 indicates petroleum inputs, 0.20-0.35 indicates a mixed sources (either petroleum or combustion), and a ratio >0.35 indicates combustion sources. For IP/276, the ratio <0.20 indicates petroleum inputs, between 0.20 and 0.50 indicates a mixed sources, and >0.50 indicates combustion of coal, grasses and wood. Beside the isomeric and molecular ratios, the homologues alkyl PAHs ratios were used; C0/(C0+C1)F/P <0.5 indicates petroleum sources and a ratio >0.50 indicates combustion sources (Yunker et al. 2002, 2012).

As shown in Table 12B, results of PAH molecular and isomeric ratios give an inconsistent picture of PAHs origins so these four diagnostic ratios seem to be inadequate for the differentiation of hydrocarbon origins in our case of the LCZ sediment samples. The dominance sources of PAHs is not similar for all used diagnostic ratios at each station except for Abou Ali estuary were all ratios used show the predominance of pyrogenic sources. Indeed, recent studies show that pyrogenic sources, characterized by the predominance of parent compounds with four or more aromatic rings derived during combustion. In contrast, petrogenic sources contain only two and/or three aromatic ring compounds derived from the direct discharges of petroleum and its products (Barakat et al., 2011; Chen and Chen, 2011). Therefore, a ratio of LMW (Nap, Acy, Ace, Fl, Phe, and Ant) to HMW (Pyr, Flu, BaA, Chr, BbF, BkF, BaP, IP, DBA and BgP) PAHs has been used to identify between these two sources were a ratio LMW/HMW <1 confirm the pyrogenic sources and a ratio >1 confirm the petrogenic sources of PAHs in sediments (table 12A) (Budzinski et al., 1997; De Luca et al., 2005). In Table 12B, the results of this ratio (LMW/HMW) show that the combustion was the predominance source of PAHs at Abou Ali estuary, Chekka Bay and Port of Beirut while the petroleum input was the predominance source at Jounieh Bay and Port of Jiyeh power plant. The ratios of Alkylated PAHs compounds (A-PAHs)/Parents PAHs (P-PAHs) have been plotted versus LMW/HMW to show the predominance sources of PAHs at each sampling stations (Fig. 22). It is interesting to note that the results of LMW/HMW ratio comply with the composition profile of PAHs described previously in this paper. Therefore, the comparative evaluation between the molecular/isomeric pairs ratios and LMW/HMW ratio indicates that this ratio can be considered a reliable tool for discriminating between petrogenic and pyrogenic origins of PAHs in this study (Sicre et al., 1987; Budzinski et al., 1997).

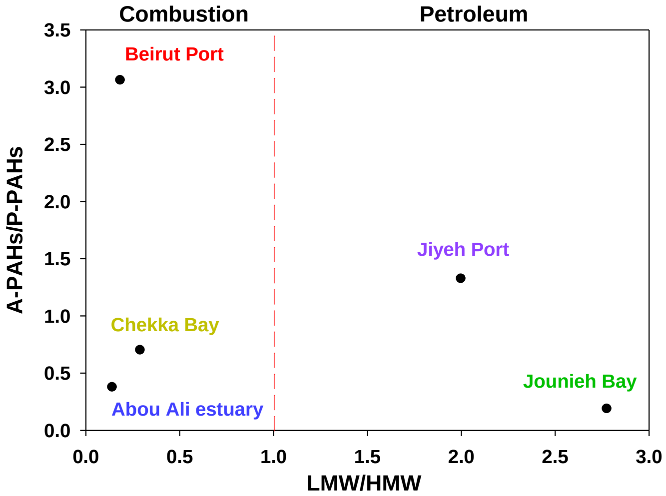

Fig. 22: PAHs cross plot for the Ratio of LMW/HMW vs. A-PAHs/P-PAHs: sum of alkylated PAHs concentrations against sum of non-alkylated (parent) PAH concentrations. The dash line represent the threshold for ratio LMW/HMW.

LCZ is subject to high contamination by PAHs mainly due to the urbanization and industrial development in this zone. For Beirut Port, the combustion were defined as the predominance sources of PAHs mainly resulting from ships engine emissions, port equipment (e.g. winches, forklifts), maritime transport or shipping activities, vehicles traffic (highway), diesel trucks (Transit activities) and dust generated from rehabilitation and construction activities (Mostert et al., 2010; Tobiszewski and Namieśnik., 2012; Feng et al., 2012; Borgie et al., 2015). Moreover, the capital Beirut has a high density of population suggesting that exhaust emissions from vehicles and burning of wood and biomass may contribute to PAHs pollution in this area as well as for Abou Ali River, which pass through Tripoli city second largest city in Lebanon. In fact, POPs prone to long range transport via atmospheric route which has been identified as the key global dispersal mechanism for most legacy POPs including PAHs and PCBs. Accordind to Wania (2003) these POPs can be classified as flyers, multi-, single hoppers and swimmers. A number of emerging POPs may not fall into the same multimedia region (Lohmann et al., 2007). Whereas, PAHs act as “single hoppers” suggesting that Beirut Port can be affected by the emissions released from surrounding industries and power plant such as the case of Jiyeh power plant which is located at 30 km away from the capital. For Chekka Bay, the dominance of combustion process can be explained by the presence of two cement factories. In addition to being an industry leader on the Lebanese market, the company is also a prominent worldwide cement exporter, serving the Levant, Africa and occasionally Europe. Harbors activities are reserved essentially for the import of coal, petroleum products, slag and gypsum and the export of clinker and cement. Due to their location in the coast have an important access to the regional markets in the Mediterranean basin through this port leading to an important production, transport and shipping activities which often increase the risk of pollution by toxic chemicals in particular PAHs released during combustion process and the emission of coal/coke dust. Although, the presence of these important sources of pollution at Chekka Bay the level of contamination is less than at Port of Beirut reaching 552.4 $\mu g.kg^{-1}$ dw, this area is well covered by long trees and high mountains regions suggesting that play as a traps for these contaminants (Grimalt et al., 2001; Daly and Wania, 2005). For Port of Jiyeh power plant, the petrogenic sources was the predominance sources of PAHs in sediments mainly released from the direct inputs of petroleum product in particular the oil spillage event occurred during the conflict with Israel in July 2006, shipping activities, oil loading/unloading operations, oil leaks or spills from pipelines, tanks and ships, ships discharges and cooling water taken from the Sea and let into the Sea (Luca et al., 2004; Huang et al., 2011). For Jounieh Bay the predominance of petrogenic sources mainly related to the urban runoffs, sewage discharges, fishery and touristic activities there were many boats travelling in the bay and yachts centre hence there are many nonpoint sources contributing to petrogenic PAHs contamination (Zhou and Maskaoui, 2003).

Sources identification of PCBs in environment is a challenge, PCBs data are the most highly diversified and difficult to interpret (konat and Kowalewska, 2001) because no diagnostic ratios of PCBs congeners can be found in the literature like that used for PAHs. Following, the ban on PCBs production in 1970s, PCBs still present at trace levels in marine environment (Ross. 2004). Therefore, we should to note that some equipment and materials containing PCB is still in use in some region in the world (Ross. 2004) (e.g. capacitors, concrete coatings, and double framed glazing windows, vessels paints, exterior paint from building façades and building materials (Andersson et al., 2004). Moreover, it is interesting to mention that continuing PCBs emissions in densely populated areas (Jaward et al., 2004) not only attributed to the volatilization processes from soils, equipment and building materials but also formed during thermal processes (Schoonenboom et al., 1995; konat and Kowalewska, 2001; Ishikawa et al., 2007; Lohmann et al., 2007) mainly related to industrials (Hong et al., 2005; Arieset al., 2006; Liu et al., 2009), waste incineration (Shibamoto et al., 2007), vehicle exhaust (Brož et al., 2000) and combustion of organic matter (Kjeller and Rappe, 1995; Rose and Rippey, 2002; Rose et al., 2004). PCBs are classified as multi-hoppers compounds (Wania. 2003, 2006). Therefore, the detection of these pollutants in coastal sediments suggests an efficient delivery of these multi-hoppers compounds via atmospheric deposition due to gaseous exchange across the air/water interface process, dry deposition of airborne particulate matter, by rainfall, storm water runoff (Dickhut and Gustafson, 1995; Dickhut et al., 2000; Tsai et al., 2002; Oros et al., 2006) and via riverine input (konat and Kowalewska, 2001). Whereas, PAHs and PCBs have similar physico-chemical properties like hydrophobicity, persistence, long-range transport and are removed from water column by sedimentation, accumulation into food webs and volatilization processes (Lohmann et al., 2007). For these reasons, Fernández et al., (2012) and Duan et al., (2013) suggest to take into consideration the correlation between PAHs isomers and PCBs congeners for sources identifications. The composition of PCBs in sediments can provide the information on environmental origin, transport and fate processes (Li et al., 2009). 5 Cl CBs was produced as paint additive (Mai et al., 2005) so the predominance of 5 Cl CBs (56.95 %) detected in the sediments of Beirut Port and other ports indicates that paint constitute one of the important sources of PCBs. Therefore, the rehabilitation and demolition of buildings surrounding mainly are the major source of PCBs in coastal sediments at Beirut Port (Jartun et al., 2009). Other PCBs congeners with ≥6 Cl atoms detected in sediments at Port of Beirut station could be originated from unintentionally atmospheric deposition released from port equipment, generators, ships, vehicles and trucks exhaust. Jiyeh power plant contribute to the dominance of 4-6 Cl CBs and the cement factories at Chekka Bay contribute to the dominance of 7 and 9 Cl CBs. Fishery and touristic activities at Jounieh bay resorts lead to the dominance of high chlorinated PCBs with 8-9 Cl CBs which release probably from fishery boat, yachts engine and vehicle exhaust emissions surrounding.

The riverine input of Abou Ali estuary with the predominance of 7 Cl CBs which may be related to continuing diffusive atmospheric emissions in populated area (Jaward et al., 2004c) unintentionally released from vehicles exhaust and the combustion of organic matter (Kjeller and Rappe, 1995; Rose and Rippey, 2002; Rose et al., 2004) which occurred frequently in Tripoli plain and villages where the river pass through. PCBs contamination is linked to population density at Beirut Port, which is located in the capital. Based on these findings, PCBs contamination is not only the historic problem but there may have continuous emissions from urban and industrial regions along LCZ leading to this high contamination of coastal sediments. The current source of PCBs could be the volatilization from paints and building materials as the case of Beirut Port, and combustion process at Chekka Bay, Jiyeh power plant and Abou Ali estuary (Hsu et al., 2003; Uraki et al., 2004).

Toxicity and risks assessment

Toxicity risk assessment constitute an important phase for the management of PAHs and PCBs pollution in marine ecosystem. First, the evaluation of potential toxicity was performed based on the calculation of total concentration of potentially carcinogenic PAHs (C-PAHs; BaA, Chr, BaP, BbF, BkF, IP, and DBA) (Nadal et al., 2004; Qiao et al., 2006; Sprovieri et al., 2007; Lee et al., 2010; Tian et al., 2013) and PCBs-DL. The concentrations of C-PAHs at all investigated stations are presented in Table 13.

Table 13: C-PAHs, sum of six PCBs-DL, sum of 12 PAHs, TEQ PAH, TEQ PCB, SQGQ PAH and SQGQ PCB for all sampling stations along LCZ.

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

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

The highest C-PAHs concentration was determined at Port of Beirut reaching 2370 µg.kg^{-1} dw and accounting for 62.8 % of total PAHs. The lowest C-PAHs concentration was found at Port of Jiyeh power plant reaching 125 µg.kg^{-1} dw and accounting for 22.7 % of total PAHs. Among these C-PAHs, BkF and IP was the predominance compounds at all stations, which represent 25.7 and 21.4 %, 25.8 and 29.4 %, 37.6 and 32.0 % and 31.4 and 23.6 % at Abou Ali estuary, Chekka Bay, Jounieh Bay and Port of Jiyeh power plant respectively. Except at Port of Beirut, BaA and BbF was the predominance C-PAHs with 21.9 and 19.7 %. PCBs-DL are classified into three categories: non-ortho PCBs, with high concern of dioxin-like effects; mono-ortho substituted PCBs, with a weak ability to produce dioxin-like effects; and multiple-ortho substituted PCBs, with no dioxin-like effects (Ma et al., 2009; Tian et al., 2013). In this study we take great concern for six PCBs-DL (non-ortho PCBs: PCB-77 and 81; mono-ortho PCBs: PCB-105, 114, 118, and 167) due to their toxicological properties similar to 2,3,7,8-tetrachlorodibenzo- p-dioxin (2378-TCDD) (Kannan et al., 1989; Giesy et al., 1998; Nakata et al., 2003). The highest concentration of $\sum_6$PCBs-DL was detected also at Port of Beirut reaching 627 µg.kg^{-1} dw and accounting for 48.10 % of total PCBs and 63.39 % of $\sum_{12}$DL-PCBs (Table 13). The lowest concentration of $\sum_6$PCBs-DL was occurred at Jounieh Bay reaching 13 µg.kg^{-1} dw and accounting for 9.24 % of total PCBs and 51.07 % of $\sum_{12}$PCBs-DL. The $\sum_6$PCBs-DL is >50 % of $\sum_{12}$PCBs-DL at all investigated stations were represent respectively 95.47, 63.39, 71.77 and 55.52 % at Abou Ali estuary, Port of Beirut, Port of Jiyeh power plant and Chekka Bay. Therefore a great concern should be to take into consideration for these pollutants during pollution management.

The highest concentration of non-ortho PCB-77 was determined at Port of Jiyeh Power Plant (54 µg.kg^{-1} dw or 45.05 %). In the other hand, three mono-ortho PCBs congeners (PCB 118, 105 and 167) are dominant for other sampling stations accounting 219 µg.kg^{-1} dw (82.68 %) and 36 µg.kg^{-1} dw (91.91 %) for CB 167 at Abou Ali estuary and Chekka Bay, and 329 µg.kg^{-1} dw (52.53 %) and 4 µg.kg^{-1} dw (27.51 %) for CB 105 at Port of Beirut and Jounieh Bay, respectively. Moreover, the quantification and evaluation of potential toxicity of sediment was performed by calculation the total toxic equivalent quantity (TEQ carc) (Savinov et al., 2003; Nadal et al., 2004;Qiao et al., 2006; Chen and Chen. 2011) and sediment quality guideline quotient (SQGQ) (Tian et al., 2013). The TEQ carc was calculated for all C-PAHs and six PCBs-DL using the following equation (1) (Shen et al., 2010; Tian et al., 2013):

$$TEQ\ carc = \sum_i Ci \ \times TEF \overset{carc}{\underset{i}{}} \qquad (1)$$

Where, Ci is individual C-PAHs or PCBs-DL concentration (µg.kg^{-1} dw); TEF carc (toxic equivalency factors) is the toxic factor of carcinogenic PAHs relative to BaP because BaP is the only PAH for which toxicological data are sufficient for derivation of a carcinogenic potency factor (Peters et al., 1999). Whereas, TEFs for BaA, Chr, BbF, BkF, BaP, IP, and DBA are 0.1, 0.001, 0.1, 0.01, 1, 0.1, and 1, respectively, according to the US Environmental Protection Agency (US EPA, 1993). In addition, the World Health Organization (WHO) has been developed a suit of TEFs for six PCBs-DL are 0.0001; 0.0003; 0.00003 for PCB 77, PCB 81 and PCB 105, 114, 118 and 167, respectively (Tian et al., 2013). In this study, TEQ PAHs are ranged from 59 to 872 µg TEQ. kg^{-1} dw (Table 13). The maximum value of TEQ PAHs was found at Port of Beirut indicating the presence of local sources related to shipping and transport activities occurred in the Port (Sprovieri et al., 2007) causing a great impact on coastal species in this basin. The minimum value was found at Jounieh Bay indicating that touristic activities have a minor contribution of TEQ PAHs due to the dominance of petrogenic PAHs at this station with LMW which are susceptible to the dissolution, biodegradation and desorption processes during transport (Tian et al., 2013). Among C-PAHs, the DBA has a major contribution of TEQ PAHs at Abou Ali estuary, Chekka Bay and Port of Beirut accounting for 49.62 %, 49.19 % and 45.43 % respectively. While carcinogenic BaP has a major contribution of TEQ PAHs at Jounieh Bay and Port of Jiyeh Power Plant accounting for 80.88 % and 64.11 % respectively (Fig. 23a). Based on these findings, we suggest that the major contribution of DBA in TEQ PAHs mainly related to the dominance of pyrogenic sources of PAHs in Abou Ali estuary, Chekka Bay and Port of Beirut. In contrast, the major contribution of BaP in TEQ PAHs for the remaining stations mainly related to the dominance of petrogenic sources of PAHs. TEQ PCB are ranged from 0.002 to 0.019 µg TEQ. kg^{-1} dw (Table 13). The highest TEQ PCB was determined also at Port of Beirut located in the capital, where occurred intensive shipping and industrial activities into harbour with high density population in this city. The non-ortho PCB 81 contributed to highest TEQ PCB at Port of Jiyeh power plant (55.23 %) and the mono-ortho PCBs 118 and 105 have a major contribution of TEQ PCB at Port of Beirut (47.47 %) and CB 167 has a major contribution at Abou Ali estuary (82.68 %) (Fig. 23b). However, TEQ PAH and TEQ PCB showed the highest values at Port of Beirut followed by Abou Ali estuary (Table 13) indicating that the largest contribution of TEQ carc in Lebanese coastal sediments came from harbor and/or industrial activities and riverine input. Therefore, during risk assessment and pollution management, more attention should focused on PAHs and PCBs congeners with high TEQ contributions, rather than only the congeners with high concentrations.

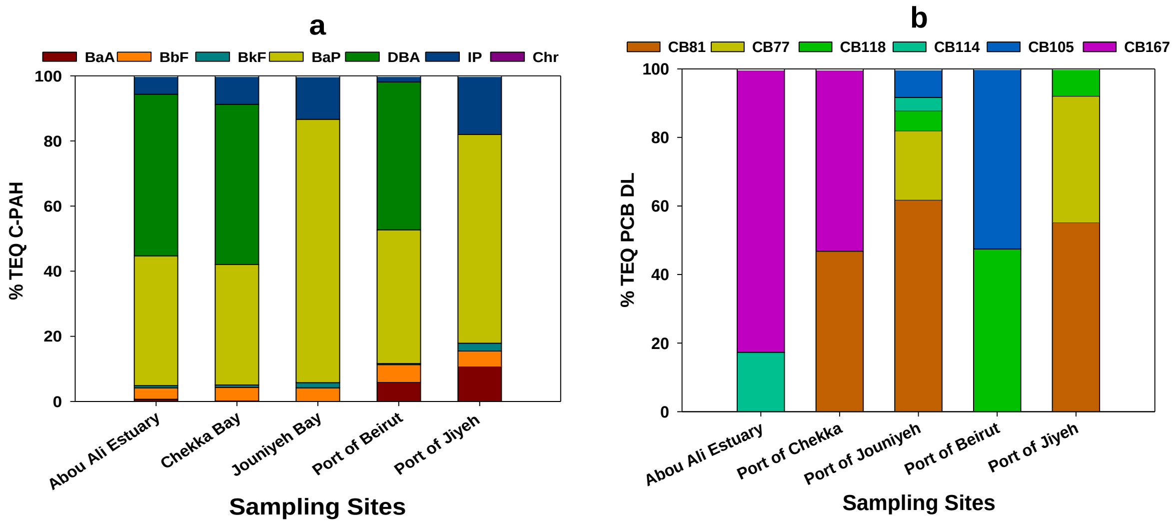

Fig. 23: Percentages of TEQ for individual **(a)** C-PAH and **(b)** six PCB-DL congeners (μg TEQ.kg-1 dw).

In addition, several tools have been developed to assess the potential adverse biological effects of the sediments at sites affected by contaminant mixtures (Long et al., 1998). The Sediment quality guidelines (SQGs) established by US National Oceanic and Atmospheric Administration (NOAA) is widely used to estimate the potential biological adverse effects of PAHs and PCBs contamination in marine and estuarine sediments (Long et al., 1995; Quiroz et al., 2010; Wang et al., 2015), based on two effective approaches designed ERL/ERM values (effects range low and effect range median) developed by Long et al., (1995) and TEL/PEL values (threshold effect level and probable effect level) developed by MacDonald et al., (1996). Three ranges of concentrations are used in the classification of biological adverse effects were expected rarely (<ERL/TEL), occasionally (≥ERL/TEL and <ERM/PEL) and frequently (≥ERM/PEL) (Long et al., 1995; Cardellicchio et al, 2007). The concentrations of $\sum_{12}$PAHs and $\sum_{28}$PCBs obtained from all investigated stations along LCZ were compared to ERL/ERM and TEL/PEL values in SQG. For all stations, the biological adverse effects of PAHs can be expected rarely according to ERL/ERM values. The concentrations of $\sum_{12}$PAHs were below ERL while these biological adverse effects are rarely expected at Abou Ali estuary, Chekka Bay and Port of Jiyeh power plant and would occur occasionally at Jounieh Bay and Port of Beirut according to TEL/PEL values (655/6676 $\mu g.kg^{-1}$ dw). In contrast, the biological adverse effects of PCBs can be expected frequently for all stations except for Jounieh Bay, which expected to occur occasionally according to the both approaches values ERL/ERM and TEL/PEL.

Furthermore, mean sediment quality guideline quotient (mSQGq) including mean ERM quotient (mERMq) and mean PEL quotients (mPELq) were applied in this study for deep evaluation of synergic effects of contaminants in sediments (Long and MacDonald, 1997; Long et al., 2006; Cardellicchio et al., 2007) then obtain a clear picture of the potential biological adverse effect at each station along LCZ. Briefly, mSQGq is calculated by dividing the individual concentrations of PCBs and 12 PAHs in sediments by their respective ERM and PEL values in SQG then calculating the mean of the quotients for all contaminants at each station following these two equations (Long et al., 1998; Bícego et al., 2006; Cardellicchio et al., 2007):

$$ERMqi \text{ or } PELqi = \frac{Ci}{ERMi \text{ or } PELi} \qquad (2) \qquad mERM\text{or } PELq = \frac{\sum_{i=1}^{n} ERMqi \text{ or } PELqi}{n} \qquad (3)$$

Where ERM and PEL is the SQG value for the contaminant i and Ci is the measured concentration of the same contaminant and n is the total number of analysed contaminants (nPAHs = 12 and nPCBs = 28) whose sediment quality guidelines are available.

This SQGq index defines four levels associated to the potential biological adverse effects: highest (mERMq >1.5 and mPELq >2.3), medium-high (mERMq ranged from 0.51 to 1.5; mPELq ranged from 1.51 to 2.3), medium-low (mERMq ranged from 0.11 to 0.5; mPELq ranged from 0.11 to 1.5) and lowest (mERMq <0.11 and mPELq <0.11) (Cardellicchio et al., 2007). Table 13 indicates that the potential biological adverse effect of PAHs and PCBs are ranged from low to medium - low for all investigated stations along LCZ. These results were in agreement with distribution pattern of PAHs and PCBs for all stations indicating that the most polluted sites was strongly influenced by harbor and power plant activities due to the limited water circulation and exchange with open sea in closed basins. Although, the influence of cement factories at Chekka Bay the effects were considered low for both PAHs and PCBs confirming our hypothesis that long trees and high mountains regions surrounding this bay play as a traps for these contaminants thus reducing their impact on aquatic ecosystem.

Conclusion

This is the first assessment study of organic contamination in surface sediments of Lebanese coast. This work has provided data on the levels of PAHs, Me-PAHs and PCBs in sediments of several hotspots zones located along LCZ extending from the north to south Lebanon including Abou Ali estuary, Chekka and Jounieh Bay, Port of Beirut and Port of Jiyeh power plant. The highest contamination of PAHs, Me-PAHs and PCBs were localized at Port of Beirut located in densely populated area and subjected to multidisciplinary activities including industrial inputs, intensive shipping and transport activities. This indicate a strong influence of the anthropogenic activities on the level of PAHs and PCBs in coastal sediments, but this significant contamination is not related to the vicinity of the most probable sources of pollution only, but in area of intensive sedimentation and limited water circulation. High mountains regions play as traps of these contaminants by reducing their fate in coastal sediments such as the case at Chekka bay where we observed clearly that the impact of cement factories and harbor activities is limited. According to Baumard et al., (1998a), the classification of PAHs pollution levels it could be considered as moderate for all sampling sites except for Port of Beirut which is highly polluted with PAHs. The composition profile study of pollutants provide a valuable information in source identification were the results show the abundance of PAHs with MMW and HMW at Abou Ali estuary, Chekka Bay and Port of Beirut sediments while PAHs with LMW are greater represented at Jounieh Bay and Jiyeh power plant. The use of different diagnostic ratios gives an inconsistent picture of PAHs origins and seem to be inadequate for the differentiation of hydrocarbon origins. Only the ratio (LMW/HMW) can be considered a reliable tool for discriminating between petrogenic and pyrogenic origins of PAHs in our study confirming that pyrogenic processes was the predominance source of PAHs at Abou Ali estuary, Chekka Bay and Port of Beirut characterized by the abundance of PAHs with MMW and HMW while the petrogenic was the predominance source at Jounieh Bay and Port of Jiyeh power plant characterized by the abundance of PAHs with LMW. For PCBs, LCZ is polluted by higher chlorinated congeners characterized by the abundance of Medium to High chlorinated PCBs with the content varying from 4 to 9 chlorine atoms. No diagnostic ratios of PCBs congeners can be found in the literature. The source identification of PCBs based upon an interpretive analysis method of literature results and composition profile congeners suggesting that atmospheric deposition is a primarily source of PCBs emissions in urban and industrial regions along LCZ. The evaluation of potential toxicity of PAHs and PCBs-DL was performed based on the calculation of TEQ carc of C-PAHs and six PCBs-DL and SQGQ. TEQ_{PAHs} and TEQ_{PCBs} suggest a relatively elevated level of toxicity at Port of Beirut followed by Abou Ali estuary indicating that the largest contribution of TEQ carc in Lebanese coastal sediments came from harbor, industrial activities and riverine input. During risk assessment and pollution management great concerns should be taken to PAHs and PCBs congeners with high TEQ contributions, rather than only the congeners with high concentrations. The potential biological adverse effect of PAHs and PCBs are ranged from low to medium - low for all investigated stations along LCZ according to SQGq. This paper provide a single approach for PAHs and PCBs contamination assessment along LCZ including distribution of concentration pattern, composition profile, sources identification and toxicity risk assessment. The gathered data in this study should be used as a baseline reference concentration and risk assessment by policy and decision makers as part of a program of integrated coastal zone management on biodiversity, sediment–water quality and economic activities along LCZ in particular during future activities in gas and oil sector. A detailed study at Port of Beirut was recommended to describe deeply the potential sources and take efficient control measures of the inputs in order to improve the quality of sediments and marine environment. Further studies for other potential contaminants (i.e., heavy metals, pesticides, TBT and PCDD/Fs) also recommended to achieving the knowledge on POPs along LCZ located in the eastern basin of Mediterranean sea.

Acknowledgements

This work was financially supported by Tripoli Harbor Authority and the LASIR Laboratory of Lille 1 University. The authors would like to thank Rouba Mecsaci and Dr David Dumoulin for all the technical support and assistance.

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Article 3

Assessment of inorganic contamination in surficial Sediments along Lebanese Coastal Zone

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Paper Prepared for submission

Date

00/00/2015

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Abstract

A Characterization and assessment study was conducted for trace metals pollution in surface sediments at six sites including harbors, bays and river input along Lebanese Coast Zone (LCZ). A particular attention was given to Port of Tripoli in order to identify the main sources of trace metal pollution inside this harbor. Total metal concentrations from eighteen surface sediments were compared with those reported for the shale for five trace metals (Cd, Zn, Pb, Cr and Co) were found exceeded the values at four sites, suggesting that LCZ is mainly affected by harbor and touristic activities and rivers inputs. Port of Beirut was found the most polluted site with the contribution of Zn and Pb. Very good agreement was found between the results of SFE and I_{geo} evaluation. The results revealed that the contamination with the anthropogenic trace metals (Cd, Pb, Zn and Cr) was significantly localized at Port of Beirut, which is classified as the most highly polluted site. At Tripoli Port site, metal contamination was classified as moderately indicating that the harbor basin was significantly affected by shipping, ship maintenance activities and sewage outfall. According to the SQGs, the biological adverse effect of Cd, Pb and Zn were expected to occur frequently at Port of Beirut while Cr and Ni were expected to occur occasionally whereas at Port of Tripoli were expected to occur occasionally for the samples collected from the corner of the old basin, close to ship maintenance area and sewage outfall. The Results obtained from this study would be helpful in developing more effective harbor management strategies to control and monitor the metal discharges into Tripoli Harbor basins and detailed study is recommended to Port of Beirut in order to take the suitable decisions regards the metal pollution. The proper treatment of industrial effluents and municipal wastewaters is the better strategy for metal pollution limitation and control.

Keywords: Trace metals, sediments, Pollution, LCZ, SEF, Igeo.

Introduction

Some ubiquitous chemicals were found at trace levels have an adverse effect on the aquatic ecosystem and human health if reached toxicity threshold (MacDonald et al., 1996; O'Connor, 2004; Islam et al., 2004; Lin et al., 2013). Among these chemicals, heavy metals are a group of pollutant of high ecological significance (Çevik et al., 2009) due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviors (Duman et al., 2007; Rui-lian et al., 2008; Liang et al., 2011; Lenoble et al., 2013). Indeed, there is a strong and long history of association between metals and human development (Tiller, 1989). Population growth, increasing urbanization, industrialization and tourism are the reasons for the increasing pressure in coastal areas (Clark, 2001; Islam et al., 2004; Roussiez et al., 2006; Buccolieri et al., 2006) were several studies have reported that are greatly contaminated by these pollutants (Buccolieri et al., 2006; Naser et al., 2013; Wang et al., 2013). Nevertheless, metal contamination along coastlines varies with the local economic development, pollution sources and geographical conditions (Pan and Wang, 2012b). In Mediterranean Seacoast, sediments have different geochemical composition where metal concentrations vary according to the area and different inputs from the coastal environment (Buccolieri et al., 2006). A significant amounts of anthropogenic heavy metals are released into marine environment (Diop et al., 2012, 2015; Memet and Bülent, 2012; Bodin et al., 2013) through land based effluent sources (Islam et al., 2004; Fu and Wang, 2011) including point sources such as industrial, municipal and domestic waste water effluents, ships discharges, river inputs as well as diffuse sources such as surface runoff, erosion and atmospheric deposition (Salomons and Forstner, 1984; Rivail Da Silva et al., 1996; Karageorgis et al., 2002; Mucha et al., 2003; Islam et al., 2004; Zahra et al., 2014). More than 90% of heavy metals load in the aquatic ecosystems has been found to be associated with suspended particulate matter and sediments by particle surface absorption, ion exchange, co-precipitation, and complexation with organic matter (Tessier and Campbell, 1987; Amin et al., 2009; Zheng et al., 2008; Passos et al., 2010). Sediment act as a sink for both organic and inorganic pollutants including heavy metals (Ruilian et al., 2008) providing a history of pollution pattern (An et al., 2003; Casas et al. 2003; Singh et al. 2005; USEPA, 2005) and record of anthropogenic pollutants input into aquatic ecosystems (Mwamburi 2003; Santos Bermejo et al., 2003; USEPA, 2004; Lesven et al., 2010) and environmental changes (Shomar et al., 2005). Their bio-accumulation and bio-magnification in living organisms and food chains causing the degradation of marine ecosystem by reducing species diversity which led in consequence to a potential hazard effects to aquatic life (Manahan, 2000; Muhua et al., 2003; Ghrefat and Yusuf 2006; Khaled et al. 2006; Hosono et al., 2011; Rainbow and Luoma, 2011). In addition, many heavy metals are known to be toxic or carcinogenic to humans causing also a great threat to public health (Islam et al., 2004; Fu and Wang, 2011). The toxicity of trace metals take more concern considering the reason that they are not removed from water and sediments by self-purification (Harikumar et al., 2010). Therefore, the evaluation of ecological risk becomes a hot topic (Lesven et al., 2009; Mario, et al., 2012). In the other hand, these heavy metals immobilized in the bottom sediment becoming bioavailable since they can be released to the overlying water as a result of physicochemical changes either due to natural and/or anthropogenic processes contributing to a permanent sources of pollution (Tessier and Campbell, 1987; Lacerda et al., 1992; Sahuquillo et al., 2003; Santana et al., 2007; Gao et al., 2010; Hooda, 2010; Morelli et al., 2014). The oxidation of anoxic sediments had reported by numerous studies as the most effective factor capable of mobilizing trace metals adsorbed in sulfide fraction (Morse 1994; Gagnon et al. 1995; Simpson and Batley 2003; Massolo et al. 2012; Dhanakumar et al. 2013) and organic phase (Calmano et al. 1993; Hamzeh et al., 2014). Many mechanisms enhanced sediment oxidation including microbial oxidation of bottom sediments, organic matter degradation, bioturbation (Simpson et al. 1998; Williamson et al. 1999), even tidal currents, erosion, seasonal flooding, wind waves, storm events, ship traffic, remedial dredging (Je et al. 2007), fishing, reclamation and construction activities (Eggleton and Thomas 2004; Guerra et al., 2009; Hedge et al., 2009) with respect to changes in geochemical gradients (e.g., salinity, turbidity and redox conditions) (Zoumis et al . 2001 ; Caetano et al. 2002; Masson et al. 2006) can strongly influence the partitioning of metals between the dissolved and particulate phases by increasing the competition between dissolved cations and adsorbed heavy metal ions lead to the increase release of these metals (Förstner et al., 1979; Hamzeh et al., 2014). Thus, their remobilization from contaminated sediment pose also a significant danger towards the aquatic environment (Zoumis et al., 2001; Eggleton and Thomas, 2004; Dean and Scott, 2004). Wherefore, sediments quality are widely used as a tool to understand current water pollution by heavy metals and assess their potential ecological risk in coastal ecosystems (Sayadi et al., 2010; Birch et al., 2001; Wang et al., 2005; Bellucci et al., 2002; Solomons and Förstner, 1984; Zonta et al., 1994). In Lebanon, the contamination of the marine sediments by heavy metals has been subjected to several studies indicating the presence of hot pollution levels in sediments near big cities and industrialized coastal zone (Abi-Ghanem et al., 2013). Also, they have indicated the need for a continuous and full Lebanese coastal monitoring to detect contamination and to take appropriate preventive measures (Abi-Ghanem, 2008; Fakhri, 2005; Nassif, 2004). The aims of this study was to investigate the levels, distribution and source identification of some trace metals in sediment samples collected from six stations along Lebanese coastal zone (LCZ), to quantify the extent of metal pollution by calculating sediment enrichment factor (SEF) and geo-accumulation index (I_{geo}) and conduct an ecological risk assessment using sediment quality guidelines (SQG).

Materials and Methods

Sampling sites

The assessment of organic contamination in superficial coastal sediments at some hotspots areas along LCZ was carried out previously by Merhaby et al., (2015). More data about inorganic pollutants are needed also in order to clarify the trend of trace metal pollution in these regions. A particular interest were given for the most exposed regions such as ports, bays and estuaries where the accumulation of trace metals is enhanced in enclosed and semi-enclosed areas where the exchange of water with the open sea is limited (Okay et al., 1996; Karageorgis et al., 2002; Pekey et al., 2004). The selected sampling stations are Port of Jieh Power Plant, Port of Beirut, Jounieh bay, Chekka bay, Abou Ali estuary and Port of Tripoli, which extend from the south to the north covering about 110 km of LCZ. Fig. 24 shows the locations of these sampling stations.

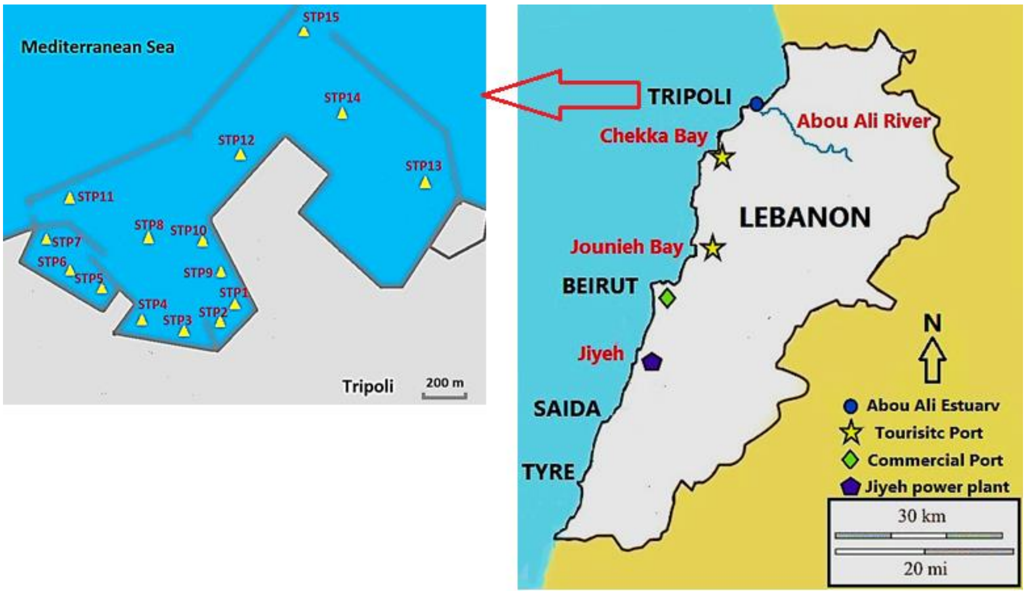

Fig. 24: Map of Studied Sampling Stations along LCZ.

Sampling strategy

Two sampling campaigns was performed, the first one was in December 2013 at Tripoli Port were 13 superficial sediment samples (top 5 cm) was collected from different stations into Port basins influenced by various activities (Fig. 24). The second one, in May 2014, at each sites three superficial sediments samples (top 5 cm) was collected as following Port of Jieh Power Plant, Port of Beirut, Jounieh bay, Chekka bay and Abou Ali estuary by diver using plastic tubes. Six sampling sites were surveyed in this study and a brief description of their characteristics is reported in Table 14.

Table 14: Description of all sampling sites at Port of Tripoli basins and five other studied sites along LCZ.

Site name	Stations	Coordinates	Depth (m)	Description	
1th campaign in December 2013					
Tripoli Port	SPT1	34°27'9.42"N 35°49'35.79"E	8	Old basin	Loading/unloading of scraps and Touristic vessels in the corner of old basin
	SPT3	34°27'5.61"N 35°49'22.72"E	2.5	Old basin	Sewage outfall in old basin
	SPT4	34°27'6.09"N 35°49'12.36"E	2.5	Old basin	Ships maintenance in old basin
	SPT5	34°27'12.26"N 35°49'5.49"E	1.8	Fishery basin	fishery basin
	SPT6	34°27'15.66"N 35°48'56.75"E	2	Fishery basin	fishery basin
	SPT7	34°27'22.85"N 35°48'52.74"E	1.8	Fishery basin	fishery basin
	SPT8	34°27'20.67"N 35°49'18.24"E	6	Old basin/Fishery basin	Mid of old basin and the entrance of fishery basin
	SPT9	34°27'15.53"N 35°49'31.50"E	8	Old basin	Loading/unloading of Cargos in old basin
	SPT11	34°27'29.62"N 35°48'58.36"E	6	Old basin	Before breakwater of old basin
	SPT12	34°27'35.09"N 35°49'35.19"E	15	New basin	Future basin for container trade
	SPT13	34°27'28.96"N 35°50'18.56"E	16	New basin	Near landfill
	SPT14	34°27'45.37"N 35°50'0.86"E	16	New basin	Between new basin and landfill
	SPT15	34°28'0.08"N 35°49'49.64"E	16	New basin	Ships entrance
2nd campaign in May 2014					
Port of Jiyeh Power Plant	SPJ1	33°38'53.85"N 35°23'53.50"E	4	Commercial harbor	Shipping activities, loading/unloading of petroleum product.
	SPJ2	33°38'53.85"N 35°23'53.50"E	6		
	SPJ3	33°38'53.85"N 35°23'53.50"E	10		
Beirut Port	SPB1	33°54'18"N 35°31'16"E	2	Commercial harbor	Loading/unloading of general cargos, container operations, shipping, transportation and fishery activities with the presence of three industrial buildings.
	SPB2	33°54'18"N 35°31'16"E	3		
	SPB3	33°54'18"N 35°31'16"E	5		

Jounieh bay	SJB1	33° 58' 59"N 35°38' 59" E	4	Touristic beach resort (marina)	Touristic activities including swimming, water sports, boating and fishing and yachting center.
	SJB2	33° 58' 59"N 35°38' 59" E	6		
	SJB3	33° 58' 59"N 35°38' 59" E	10		
Chekka bay	SCB1	34°20'4.01"N 35°43'25.75"E	3	Touristic beach resort (marina)	Touristic and industrial activities due to the presence of two cement factories located about hundred meters away from this beach.
	SCB2	34°20'4.01"N 35°43'25.75"E	4		
	SCB3	34°20'4.01"N 35°43'25.75"E	7		
Abou Ali estuary	SAE1	34°27'30.16"N 35°50'29.68"E	3	Estuary	Coastal sea receives approximately 369 Mm3/year freshwater input from Abou Ali River mixed with urban and industrial wastewater directly discharged into river without treatment.
	SAE2	34°27'30.16"N 35°50'29.68"E	6		
	SAE3	34°27'30.16"N 35°50'29.68"E	9		

Each sample was homogenized before being transferred into pre-washed polyethylene (plastic) bags to prevent any oxidation and avoid metal pollution of the samples. After that were transported to the laboratory and were frozen at -20°C for few days then dried at room temperature under laminar hood until reaching constant weight. The dried sediments were finely ground to powder manually using an agate mortar. Sediment samples processing were first sieved at 224 µm to remove large particles and homogenize the mixture. In order to reduce the effect of sediment grain size on the variability of the physicochemical measurements, the particles with size less than 63 µm were collected and used for the trace metal analysis (Abi-Ghanem et al., 2009). Sediment samples were analyzed for 9 trace metals (As, Cd, Co, Cr, Mo, Ni, Pb, V and Zn) according to the protocol described by Ouddane (1990) and Lesven et al. (2010). About 200 mg of dry sediment samples and reference materials (HISS-1, PACS-2 and MESS-3) were digested with a mixture of concentrated acids 6 ml HF (40%)/6 ml HCl (37 %)/2 ml HNO_3 (65 %) (3:3:1 v/v) in Teflon tubes putted in heating bath at 100 °C for 24 h to mineralized the solid grains. Then, after evaporation, the sample was diluted to final volume of 20 ml with Milli-Q water (Milli-Q). The solutions was then filtered at 0.45 µm to eliminate the carbon residue (Lesven et al. 2010) and stored at 4 °C until analysis (Priadi et al. 2011).

In order to determine trace metals associated with the bioavailable fractions of sediment samples, which are considered as reactive fractions, we used the method of Huerta-Diaz and Morse (1990). About 200 mg of sediment was attacked during 24 h with 20 mL of 1 M HCl (37%) at room temperature with continuous agitation. After leaching, the solution was also filtered and stored at 4 °C until analysis. The individual concentrations of major and trace elements in the extracts were measured in samples using inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian, Vista-PRO axial view) or Inductively Coupled Plasma Masse Spectroscopy (ICP-MS , Thermo Electron Corporation, Element X7 Series).

Quality control and quality assurance

All chemical reagents were ultrapure and analytical grade. All solutions were prepared using ultrapure water. Ultrapure water (Milli-Q) with 18.2 M.Ω.cm-1 resistivity was produced by Millipore apparatus system. All of bottles, glassware, tube, and filtration equipment was systematically washed with nitric acid (10%) and then rinsed several times with Milli-Q water prior to use. Reagents Blanks were included in each batch of analysis. Total heavy metal concentrations were expressed in µg/g dry sediments. A certified reference materials from the National Research Council of Canada (PACS-2, HISS-1 and MESS-3) was used as standard reference material to validate the accuracy and precision of the analytical method. The recoveries of trace metals in standard materials with known concentrations were between 95 % and 105 %, which in general can be considered satisfactory.

Results and discussion

Quantification of sediment pollution

The highest trace metals concentrations were detected for the samples collected close to Port of Beirut (Fig. 26). Table 15 summarized the individual mean concentration for each trace metals analyses in sediments of all sampling stations (SAE, SPB, SPJ, SCB, SJB and SPT).

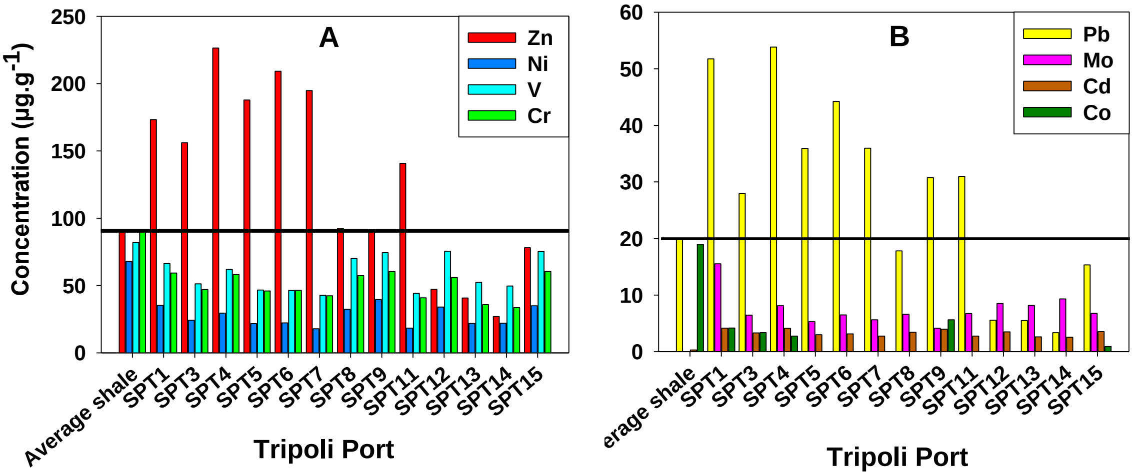

Fig. 25: Concentrations of individual trace metals Concentrations (µg/g d.w.) (**A**: Zn, Ni, V, & Cr) and (**B**: Pb, Mo, Cd, Co) in sediments collected from Tripoli Port compared with the Average shale concentrations.

Table 15: Mean Concentrations (µg/g d.w.) of individual trace metals in sediments collected from six stations distributed along LCZ.

Stations	Cr	Mn	V	Zn	Mo	Ni	Pb	Cd	Co	As
SAE	54.93	278.56	53.91	95.28	2.69	35.08	11.93	3.35	12.74	11.57
SPB	94.29	230.75	61.11	965.64	11.69	45.76	443.28	13.47	12.63	14.58
SPJ	16.93	286.42	28.28	63.24	1.33	12.59	4.64	3.06	7.37	6.71
SCB	58.62	207.24	43.18	67.29	1.77	43.30		3.77	12.09	ND
SJB	60.14	357.99	66.56	99.47	2.10	49.30	3.90	7.53	19.83	18.01
	SPT (SEDIMENT PORT TRIPOLI)									
SPT1	59.32	278.63	66.42	173.28	15.52	35.27	51.75	4.16	4.17	ND
SPT3	46.97	260.38	51.26	156.04	6.46	24.21	27.99	3.32	3.36	ND
SPT4	58.21	302.39	61.96	226.42	8.13	29.53	53.83	4.13	2.75	ND
SPT5	46.00	216.74	46.66	187.77	5.30	21.71	35.93	2.99	ND	ND
SPT6	46.50	219.77	46.30	209.19	6.50	22.29	44.23	3.13	ND	ND
SPT7	42.39	208.98	42.81	194.85	5.63	17.91	35.97	2.76	ND	ND
SPT8	57.33	231.41	70.16	92.33	6.61	32.38	17.81	3.43	ND	ND
SPT9	60.44	363.32	74.38	91.58	4.14	39.60	30.76	3.97	5.62	ND
SPT11	40.90	172.65	44.20	140.81	6.73	18.36	30.99	2.74	ND	ND
SPT12	55.89	246.57	75.56	47.23	8.51	34.06	5.57	3.49	ND	ND
SPT13	35.80	235.54	52.38	40.74	8.17	21.80	5.50	2.62	ND	ND
SPT14	33.56	224.81	49.61	26.97	9.31	22.03	3.35	2.54	ND	ND
SPT15	60.42	247.52	75.46	78.06	6.77	34.98	15.34	3.54	0.91	ND
Mean	**49.52**	**246.82**	**58.24**	**128.10**	**7.52**	**27.24**	**27.62**	**3.29**	**3.36**	**ND**
Background*	**90**	**850**	**82****	**90**		**68**	**20**	**0.3**	**19**	
ERL	**81**			**150**		**20.9**	**46.7**	**1.2**		
ERM	**370**			**410**		**51.6**	**218**	**9.60**		

**Average shale (Turekian and Wedepohl, 1961)*
*** Background value determined for Lebanese coastal sediments repoerted by Abi-Ghanem et al. (2009).*
ND: Not detected.

Referring to the concentrations of the Average shale reported by Turekian and Wedepohl, (1961) we found that the concentrations of Cd in sediments exceeded the background value for all samples collected along LCZ and Port of Tripoli. Whereas the concentrations of Zinc were found exceeded the background value at SAE, SPB, SJB, and at SPT for the following stations; STP 1, 3, 4, 5, 6, 7, 9 & 11. Pb concentrations were found above the shale value at SPB and at SPT for the stations STP 1, STP3, STP4, STP5, STP6, STP7, STP9 & STP11 (Fig. 25), while Cr and Co were exceeded the background values only at SPB and SJB, respectively (Fig. 26). Suggesting that the sediment samples collected along LCZ were polluted with Cd, Zn, Pb, Cr and Co and LCZ is mainly affected by harbor and touristic activities and rivers inputs. At Tripoli Port, the polluted sediments were collected from the fishing port and old basin of Tripoli harbor where occurred the handling and shipyards activities with the presence of sewage outfall (Fig. 25). The results show that Port of Beirut is significantly polluted with Zn and Pb with mean concentrations reach about 965.64 and 443.28 µg/g d.w., respectively (Table 15), and the comparison between these two main commercial Ports in Lebanon shows that Port of Beirut is the most polluted site.

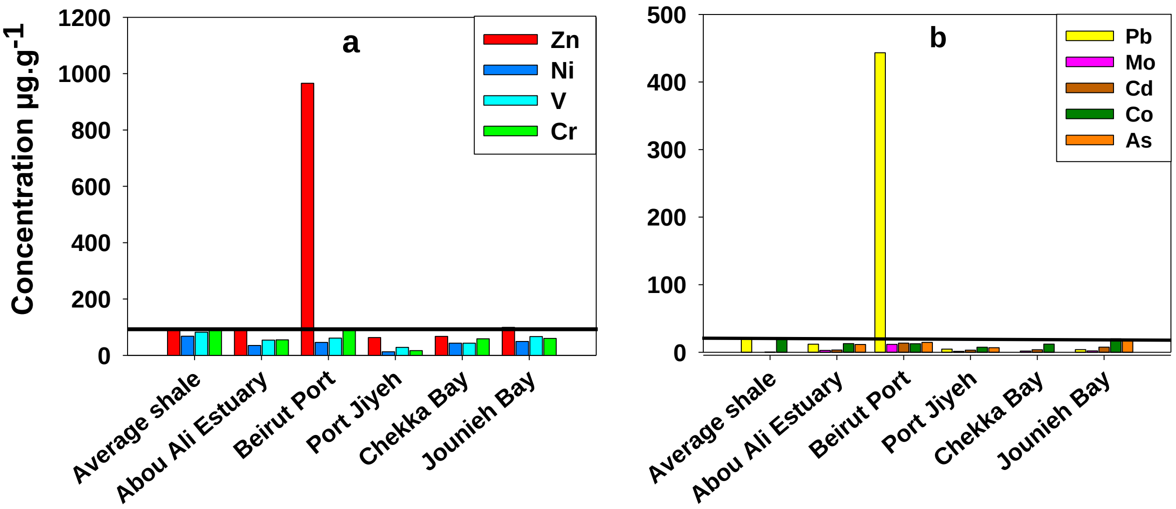

Fig. 26: Concentrations of individual trace metals Concentrations (µg/g d.w.) (**a**: Zn, Ni, V, Cr) and (**b**: Pb, Mo, Cd, Co, As) in sediments collected from five other stations distributed along LCZ compared with the Average shale concentrations.

Mobility of Trace Metals

The bioavailability is an important topic should be take into consideration during characterization of trace metals pollution in sediments particularly in semi-enclosed basins where occurred a very intensive maritime transport leading to the oxidation of anoxic sediments then the remobilization of trace metals pollutants. It was determined by calculated the percentage of mobility of each trace metals using the following equation (1):

$$\%\ of Mobility = \frac{Ci\ (AT) - Ci\ (AP)}{Ci\ (AP)} X\ 100 \qquad (1)$$

Where, Ci (AT) is the concentration of individual trace metal in sediments samples obtained after the total attack and Ci (AP) is the concentration of individual trace metals obtained after a partial attack. Table 16 shows the percentages of Mobility of each studied trace metals at each station. The percentage of mobility of almost all trace metals in sediments of the studies stations is up to 50% except for Pb, which were found the less mobile. Some exceptions were observed for Zn at SPB, which is the dominant trace metal but the less mobile (25 %) at this site. At SPT, the Zn, Co and Cd are also less mobile with percentage around 30 %, 32 % and 37 %, respectively. And, at SPJ the Mo exhibit low bioavailability characteristic with percentage around 34 %.

Table 16: Percentage of Mobility for the studied trace metals at investigated stations distributed along LCZ.

Stations	Cr	V	Zn	Mo	Ni	Pb	Cd	Co	As
SAE	79	69	64	51	69	22	96	61	100
SPB	64	49	25	75	60	16	76	64	92
SPJ	80	81	55	34	78	4	100	84	100
SCB	81	80	73	61	57		95	56	
SJB	81	77	63	48	62	100	96	55	100
OEPT	80	70	30	65	69	18	37	32	

Sediment quality assessment and intensity of pollution

Multiple evaluation methods were used to evaluate the intensity of pollution and the potential ecological risk of trace metal pollutants in sediments of the areas of investigation. In this study, three different methods were used to assess the degree of heavy metal contamination and toxicity in sediments.

Enrichment factor (EF)

Sediment Enrichment factor (EF) has widely been used to speculate the origin of a single element by differentiating between their natural and anthropogenic sources (Loska et al., 2004; Sakan et al., 2009; Guo et al., 2010; Choi et al., 2012). In this work, the EF was calculated as follows:

$$EF = \frac{Ci}{\mathrm{CAS}} \qquad (2)$$

Where, Ci is the concentration of individual trace metal in each sediment sample (µg/g d.w.) and C_{AS} is the world average concentration of individual trace metals reported for the shale by Turekian and Wedepohl, (1961). Based on EF values, all the sites were categorized into five main classes (Table 19) (Birch and Olmos, 2008). Indeed, EF value less than 1, indicate that the metal is entirely from crustal materials or natural processes while EF values higher than 1 whereas suggest that the sources are more likely anthropogenic (Buruaem et al., 2012; Diop et al., 2015). Moreover, the EF were also used to assess the degree of pollution by computing the total enrichment factor (TR) for each station by averaging the SEF values of all of trace metals analyses. Four intervals criteria were used for pollution classification at investigated sites as following: highly polluted ($TR > 3$), moderately polluted ($2.0 < TR < 3.0$), weakly polluted ($1.0 < TR < 2.0$) and unpolluted ($TR < 1$) (Adamo et al., 2005). Table 17 summarized EF values of studied trace metals and the total enrichment factor (TR) obtained at each sampling station and Table 19 represents EF and I geo classes used for sediment quality and pollution intensity assessment (Müller, 1981; Ruiz, 2001).

Table 17: Enrichment factor values of studied trace metals and the total enrichment factor (TR) obtained at each sampling station.

	ENRICHMENT FACTOR (EF)									
STATIONS	**Cr**	**Mn**	**V**	**Zn**	**Ni**	**Pb**	**Cd**	**Co**	**(TR)**	**Pollution classification**
SAE	0.61	0.33	0.66	1.06	0.52	0.60	11.17	0.67	1.77	**WP**
SPB	1.05	0.27	0.75	10.73	0.67	22.16	44.90	0.66	9.05	**HP**
SPJ	0.19	0.34	0.34	0.70	0.19	0.23	10.20	0.39	1.40	**WP**
SCB	0.65	0.24	0.53	0.75	0.64	0.00	12.57	0.64	1.81	**WP**
SJB	0.67	0.42	0.81	1.11	0.73	0.20	25.10	1.04	3.36	**HP**
					SPT					
SPT1	0.66	0.33	0.81	1.93	0.52	2.59	13.87	0.22	2.34	**MP**
SPT3	0.52	0.31	0.63	1.73	0.36	1.40	11.07	0.18	1.81	**WP**
SPT4	0.65	0.36	0.76	2.52	0.43	2.69	13.77	0.14	2.39	**MP**
SPT5	0.51	0.25	0.57	2.09	0.32	1.80	9.97	0.00	1.74	**WP**
SPT6	0.52	0.26	0.56	2.32	0.33	2.21	10.43	0.00	1.87	**WP**
SPT7	0.47	0.25	0.52	2.17	0.26	1.80	9.20	0.00	1.65	**WP**
SPT8	0.64	0.27	0.86	1.03	0.48	0.89	11.43	0.00	1.76	**WP**
SPT9	0.67	0.43	0.91	1.02	0.58	1.54	13.23	0.30	2.10	**MP**
SPT11	0.45	0.20	0.54	1.56	0.27	1.55	9.13	0.00	1.54	**WP**
SPT12	0.62	0.29	0.92	0.52	0.50	0.28	11.63	0.00	1.67	**WP**
SPT13	0.40	0.28	0.64	0.45	0.32	0.28	8.73	0.00	1.25	**WP**
SPT14	0.37	0.26	0.61	0.30	0.32	0.17	8.47	0.00	1.19	**WP**
SPT15	0.67	0.29	0.92	0.87	0.51	0.77	11.80	0.05	1.79	**WP**

WP: WEAKLY POLLUTED
MP: MODERATELY POLLUTED
HP: HIGHLY POLLUTED

The results show that the EF of Cd varied between moderately severe enrichment to extremely severe enrichment for the all of the sampling stations. The extremely severe enrichment was found at SPB and SJB with EF values about 44.90 and 25.10, respectively (Fig. 27A). Whereas EF of Pb and Zn varied between no enrichment to minor enrichment for the all of the sampling stations except at SPB were found as severe enrichment with values reach 22.16 and 10.73, respectively (Fig. 27A). For, all others trace metals (Cr, V, Ni, and Co) no enrichment was detected except for Cr at SPB where a minor enrichment was observed. Therefore, we suggest that the anthropogenic activities contribute significantly to the coastal sediment pollution with Cd, Pb, Zn and Cr particularly at Port of Beirut and Jouniyeh Bay which are classified as highly polluted sites according to the total enrichment factor (TR) (Table 17) (Fig. 27A). At Tripoli Port, the STP 1, 4 and 9 were classified as moderately polluted stations indicating the influence ship maintenance activities and sewage outfall input (Fig. 27B).

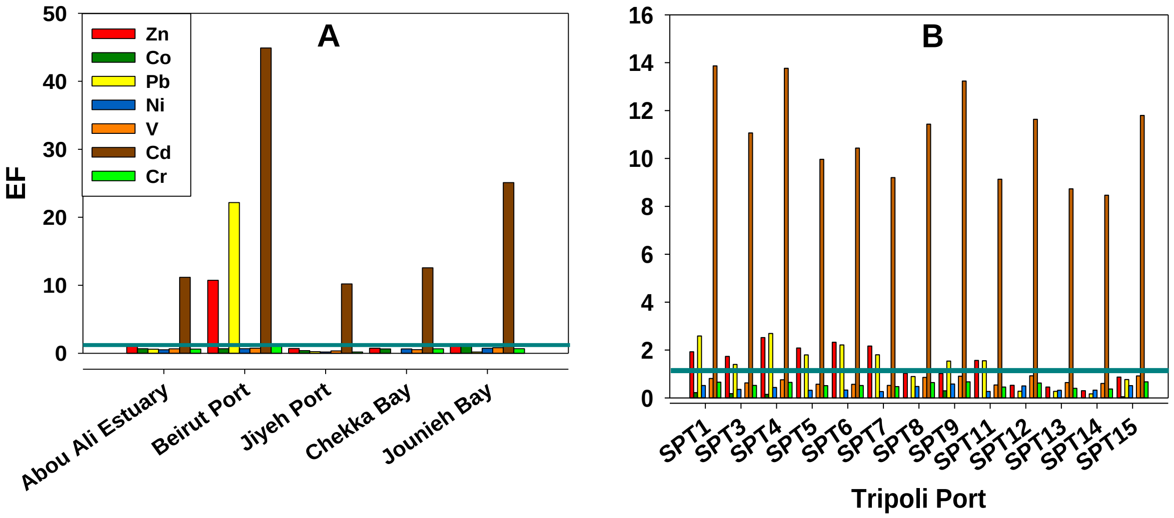

Fig. 27: Enrichment factor (EF) values of individual trace metals of (A) all sampling stations distributed along LCZ and (B) Port of Tripoli.

Geoaccumulation index (I_{geo})

Geoaccumulation index (I_{geo}) was also applied as an evaluation method to evaluate and classify the sediment quality of these sampling sites. This index was developed by Müller (1979) as a tool to evaluate the intensity of trace metal pollution in sediments and soils (V.K. Singh et al., 2005; Amin et al., 2009; Zahra et al., 2014). Igeo was calculated according to Müller and is given in equation (3).

$$\mathrm{Igeo} = \log 2\ (\mathrm{Ci}\ /[1.5].\mathrm{Bi}) \qquad (3)$$

Where, Ci is the concentration of individual trace metal in each sediment samples (µg/g d.w.) and Bi is the geochemical background value of individual trace metal in the shale by Turekian and Wedepohl, (1961) and the factor 1.5 corresponds to possible variations from the baseline due to lithological processes. The overall results of I_{geo} values shown in Table 18 were interpreted using the I_{geo} classes given in Table 19.

Table 18: Igeo values of studied trace metals obtained at each sampling station.

	GEOACCUMULATION INDEX (I_{GEO})							
STATIONS	**Cr**	**Mn**	**V**	**Zn**	**Ni**	**Pb**	**Cd**	**Co**
SAE	-1.30	-2.19	-1.19	-0.50	-1.54	-1.33	2.90	-1.16
SPB	-0.52	-2.47	-1.01	2.84	-1.16	3.89	4.90	-1.17
SPJ	-3.00	-2.15	-2.12	-1.09	-3.02	-2.69	2.77	-1.95
SCB	-1.20	-2.62	-1.51	-1.00	-1.24		3.07	-1.24
SJB	-1.17	-1.83	-0.89	-0.44	-1.05	-2.94	4.06	-0.52
	SPT							
SPT1	-1.19	-2.19	-0.89	0.36	-1.53	0.79	3.21	-2.77
SPT3	-1.52	-2.29	-1.26	0.21	-2.07	-0.10	2.88	-3.08
SPT4	-1.21	-2.08	-0.99	0.75	-1.79	0.84	3.20	-3.37
SPT5	-1.55	-2.56	-1.40	0.48	-2.23	0.26	2.73	
SPT6	-1.54	-2.54	-1.41	0.63	-2.19	0.56	2.80	
SPT7	-1.67	-2.61	-1.52	0.53	-2.51	0.26	2.62	
SPT8	-1.24	-2.46	-0.81	-0.55	-1.66	-0.75	2.93	
SPT9	-1.16	-1.81	-0.73	-0.56	-1.36	0.04	3.14	-2.34
SPT11	-1.72	-2.88	-1.48	0.06	-2.47	0.05	2.61	
SPT12	-1.27	-2.37	-0.70	-1.52	-1.58	-2.43	2.96	
SPT13	-1.91	-2.44	-1.23	-1.73	-2.23	-2.45	2.54	
SPT14	-2.01	-2.50	-1.31	-2.32	-2.21	-3.16	2.50	
SPT15	-1.16	-2.36	-0.70	-0.79	-1.54	-0.97	2.98	-4.97

Table 19: Enrichment factor (EF) and I geo classes used for sediment quality and pollution intensity assessment**.**

SEF classes	Sediment quality	I_{geo}	I_{geo} classes	Pollution intensity
SEF<1	No enrichment	< 0	0	Unpolluted
SEF<3	Minor enrichment	0 – 1	1	Unpolluted to moderately polluted
SEF 3 – 5	Moderate enrichment	1 – 2	2	Moderately polluted
SEF 5 – 10	Moderately severe enrichment	2 – 3	3	Moderately to highly polluted
SEF 10 – 25	Severe enrichment	3 – 4	4	Highly polluted
SEF 25 - 50	Extremely severe enrichment	4 – 5	5	Highly to very highly polluted
		5 – 6	>5	Very highly polluted

The results revealed that the degree of sediment pollution of all sampling stations was classified as moderately to highly polluted (classes 3 and 4) with Cd except for SPB where the pollution intensity was classified as high to very high (Class 5) (Fig. 28). While for Pb the intensity of sediments pollution was classified as highly polluted (Class 4) at SPB and as unpolluted to moderately polluted with Pb (Class 1) at SPT for the following samples STP1, STP4, STP 5, STP 6, STP 7, STP 9 & STP 11. And, for Zn also the degree of sediments pollution were was classified as moderately to highly polluted (Class 3) at SPB and as unpolluted to moderately polluted (Class 1) at SPT for the following samples STP1, STP 3, STP 4, STP 5, STP 6, STP 7 & STP 11. Above all, the intensity of sediment pollution at SPB was classified as highly to very highly, highly and moderately to highly polluted with Cd, Pb and Zn, respectively. At SPT, the intensity of sediment pollution was classified as moderately to highly polluted with Cd and unpolluted to moderately polluted with Pb and Zn, respectively. For all other stations, the intensity of sediment pollution was classified as moderately to highly polluted with Cr while for the remaining trace metals (Cr, V, Li, Ni, and Co) the intensity of sediments pollution was classified as unpolluted for all sampling stations. Very good agreement was found between the results of SFE and I_{geo} evaluation.

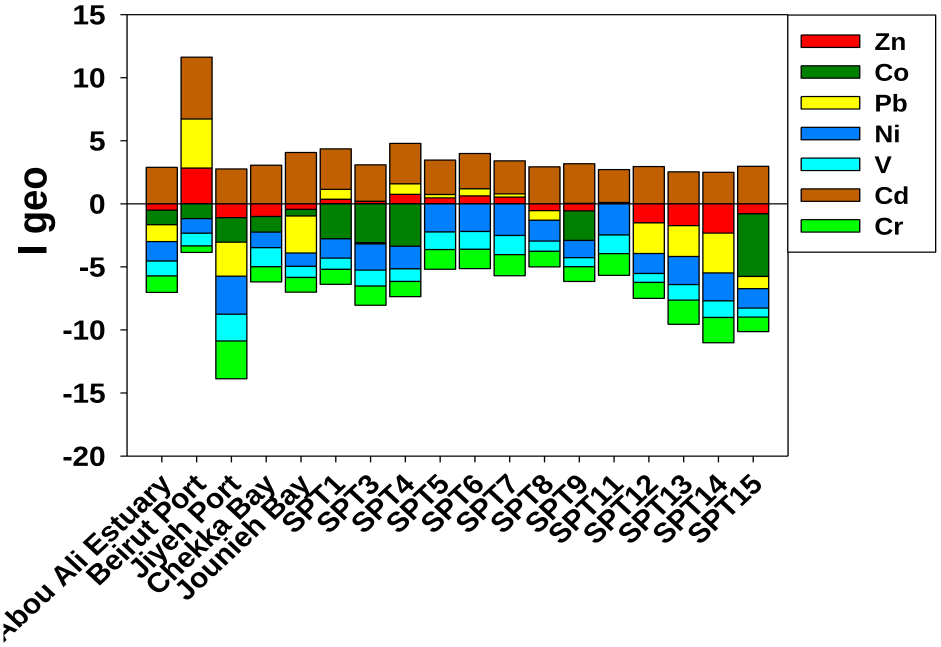

Fig. 28: I geo values of individual trace metals of all sampling stations distributed along LCZ and Port of Tripoli.

Sediment Quality Guideline (SQGs)

Another way to assess the ecotoxicological risk of sediments contaminated by heavy metal is the sediment quality guidelines developed by Bakan and Özkoç (2007) for marine and estuarine ecosystems. Long et al. (1995) identified two guideline values: the effects range-low (ERL) and the effects range-median (ERM). Concentrations < ERL value the biological adverse effect were expected to occur rarely, > ERL and < ERM were expected to occur occasionally and > ERM value were expected to occur frequently (MacDonald et al., 2000a,b). The trace metals concentrations in sediments were compared with ERL and ERM (Table 15), and the results indicate that the biological adverse effects of Cd in sediments were expected to occur occasionally for 95 % of studied stations except for SPB were expected to occur frequently. Whereas the biological adverse effects of Zn were expected to occur rarely for 61 % of sampling stations and occasionally for 33 % for those collected from Tripoli Port (STP 1, STP 3, STP4, STP 5, STP 6, & STP 7) and frequently at SPB. The adverse effect of Pb were expected to occur rarely for 82 % of sampling stations and occasionally for 12 % for those collected also from Tripoli Port (STP

1 & STP 4) affected by shipping and maintenance activities and frequently in sediments of SPB. For Cr in sediments we were expected that the adverse effects to occur rarely for all studied stations except for SPB were expected occasionally. For Ni the effects were expected rarely to 17 % of sampling stations and occasionally for 83 % while for Cr the adverse effects were expected rarely for 94 % of samples and occasionally at SPB (6%). Above all we conclude that the biological adverse effect of Cd, Pb and Zn were expected to occur frequently at Port of Beirut while Cr and Ni were expected to occur occasionally in this site whereas at Tripoli Port were expected to occur occasionally for the samples collected from the corner of old basin, close to ship maintenance area and sewage outfall.

Conclusion

Six strategic sites represent the Lebanese coast from north to south were assessed and investigated for trace metals contamination levels. A particular attention was given to Tripoli Port, which is more accessible for sampling in order to identify the main sources of trace metals in harbor. We focused in this study on the contamination levels of 9 trace metals, their mobility and their ecological risks in sediments of the studied sites. The concentrations of five trace metals (Cd, Zn, Pb, Cr and Co) were found exceeded the background values at four sites; SPB, SPT, SJB and SAE suggesting that LCZ is mainly influenced by harbor and touristic activities and rivers inputs. Port of Beirut was found the most polluted site with the significant contribution of Zn and Pb in this metal contamination. The percentage of mobility of almost all trace metals in sediments of studies stations is up to 50% except for Pb, which were found the less mobile trace metals. The results of EF show that the anthropogenic activities contribute significantly to the coastal sediment pollution with Cd, Pb, Zn and Cr particularly at Port of Beirut, which is classified as highly polluted site. At SPT, metal contamination was classified as moderately indicating that the harbor basin was significantly affected by shipping, ship maintenance activities and sewage outfall. Very good agreement was found between the results of FE and I_{geo} evaluation. The intensity of sediment pollution at SPB was classified as highly to very highly, highly and moderately to highly polluted with Cd, Pb and Zn, respectively while at SPT was classified as moderately to highly, and highly polluted with Cd and unpolluted to moderately polluted with Pb and Zn, respectively. For all other stations, the intensity of sediment pollution with Cr was classified as moderately to highly while for the remaining trace metals (Cr, Mn, V, Ni, and Co) the intensity of sediments pollution was classified as unpolluted for all sampling stations. According to the SQGs, the biological adverse effect of Cd, Pb and Zn were expected to occur frequently at Port of Beirut while Cr and Ni were expected to occur occasionally whereas at Tripoli Port were expected to occur occasionally for the samples collected from the corner of old basin, close to ship maintenance area and sewage outfall. The reduction of metal concentrations in sediments after remediate actions was insignificant and is very expensive (Chen et al., 2007) and the stable organic-metal association in the sediment complicates the engineering remediation of contaminated sediments. The Results obtained from this study would be helpful in developing more effective harbor management strategies to control and monitor the metal discharges into Tripoli Harbor basins and detailed study is recommended to Port of Beirut in order to take the suitable decisions regards the metal pollution. In general, for metal pollution control we suggest that the proper treatment of industrial effluents and municipal wastewaters is a better strategy to control the sediment metals in the harbors by reducing the released of these pollutants from the sources.

Acknowledgements

This work was supported by the Analytical and Marine Chemistry Team of LASIR Laboratory, at Lille 1 University and Tripoli Harbour Authority. The authors would like to thank Sarah Ghomraoui, Rouba Mecsaci, Nihal Gokbulak and Dr David Dumoulin for all the technical support and assistance during the prepapartion and sampling campaign.

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CHAPTER 4

TRIPOLI HARBOUR CONTINGENCY PLAN

Article 4

Tripoli Harbor Contingency Plan for a Durable Development (Lebanon)

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Paper Prepared for submission

Date
00/00/ 2015

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Abstract

Harbors can be considered as a complex and hotspot ecosystems in coastal areas where can occurred a fire accidents either onshore or offshore and can concentrate and release a large amount of any form of waste into the waters of the harbor generated from anthropogenic activities including maritime transport and shipping activities. Tripoli harbor (OEPT) in Lebanon is among the most important port on the Mediterranean Sea eastern basin aim to ensure an environmental sustainability and complying with legal duties to the management of ship-generated waste, including the requirements of MARPOL 73/78. Therefore, harbor authorities work for dealing with fire accidents and pollution generated from ship discharges, oil spillages, garbage, sewage and other hazardous substances within harbor areas by preparing a contingency plan including a fire safety management plan, oil spill emergency response plan and waste management plan. This plan is constitute from an emergency response plan for fire accidents and Oil spill containment, by providing guidance to respond for these accidents and to set in motion all necessary remedial actions in order to minimize their potential environmental and economic damage. And, some considerations should be taken into account during planning process are consultations, collecting and sharing information and the elaboration a partnership approach. Harbor authority should to familiar with key response functions; conduct a regularly exercised and periodic review to ensure the effectiveness of these plans. OEPT Contingency Plan was elaborated for long term (five years) and the best implementation of all requested actions will ensure the durable development in Tripoli harbor.

Keywords: Contingency Plan, Durable Development, Pollution, Safety, Tripoli Harbor.

Introduction

Harbors are a small cities in the cities where can concentrate a multidisciplinary activities mainly caused a significant threat to the employees, surrounding areas and environment. The statutory duties of harbor authorities relate specifically to provide a safe workplace for its staff, leaseholder and visitors and to response to pollution from ships in their waters, and land which they own (OPRC, 2012). These duties are also a commercial imperative. The serious accidents which may occurred in the harbor cannot only cause a serious disruption to the port or environment at the time, but may well have longer term impacts. It is therefore much better to work based on the principle that it is better to prevent incidents than to deal with them after they have occurred. On field, local arrangements will take a practical approach to “who does what", the important thing is the good planning in order to make the same agreed assumptions, ensure the best implementation of actions, complying with laws & regulations and for there to avoid any gaps (OPRC, 2012). Because that the sustainability development is a current concern for Tripoli Port Authority, it works to integrate an Environmental and occupational Health and Safety Management System (ISO 14001 & 18001) including all required policies and procedures which has been issued by HSE department at OEPT for those who will execute such plans and for the directors, employees, operators, contractors, transporter, shipping agencies, stakeholders, and others responsible for its legal and other functions. Moreover, a code for safe practices was elaborated by Consultant Company to assist harbor authority to develop such plans or systems and to manage their operations thereby. Indeed, this safety code is a part of OEPT Contingency Plan includes a fire safety management plan, an emergency response plan for oil spills and waste management plan. Its purpose is to ensure that there is timely, measured and effective response to incidents for long term and provide a guidance to respond for these types of accidents in order to set in motion all necessary remedial actions required to minimize their potential environmental and economic damage. The objectives of this paper are to describe planning processes, and designs and approaches used for the elaboration of OEPT fire safety management plan and OEPT oil spill response plan included in the contingency plan. As a party to the UN Convention on the Law of the Sea (UNCLOS), Lebanon has an obligation to protect and preserve the marine environment (OPRC, 2012). In addition, MARPOL 73/78 Convention defined Mediterranean Sea as a “Special Sea Area”, where the discharges from ships is entirely prohibited with only minor and well defined exceptions (Annex I for Oily waste, Annex IV for Sewage and Annex V for Garbage).The International Convention on Oil Pollution Preparedness, Response and Co-operation 1990 (the OPRC Convention) which require from harbor authorities to have a duty to prepare plans to clear oil spills from their harbor and for those plans to be compatible with the National Contingency Plan for Marine Pollution from Shipping and Offshore Installations

(NCP) but unfortunately, there is no monitoring infrastructure of such practices in Lebanon. List of IMO conventions ratified by Lebanon are summarized in Table 20 (IMO, 2015). In the Other hand, Barcelona Convention addresses the protection of specially protected areas and biodiversity in the Mediterranean Sea through the elimination of pollution from land-based sources and the establishment of marine protected areas (MAP 2005; Green Peace 2007). And, the Convention for Biological Diversity (CBD) urges Parties and other Governments to make efforts to adopt a marine and coastal management framework for marine and coastal protected areas (COP 7, 2004; CBD, 2007; Green Peace 2007).

Table 20: United Nations treaties ratified by the state of Lebanon, 17/08/2015.

United Nations treaties ratified by the state of Lebanon

X	IMO Convention 48	X	INTERVENTION Convention 69
X	SOLAS Convention 74		INTERVENTION Protocol 73
X	SOLAS Protocol 78	X	CLC Convention 69
	SOLAS Protocol 88		CLC Protocol 76
	SOLAS Agreement 96	X	CLC Protocol 92
X	LOAD LINES Convention 66		FUND Convention 71
X	LOAD LINES Protocol 88		FUND Protocol 76
X	TONNAGE Convention 69		FUND Protocol 92
X	COLREG Convention 72		FUND Protocol 2003
X	CSC Convention 72		NUCLEAR Convention 71
	CSC amendments 93		PAL Convention 74
	SFV Protocol 93		PAL Protocol 76
	Cape Town Agreement 2012		PAL Protocol 90
X	STCW Convention 78 or 70!		PAL Protocol 02
	STCW-F Convention 95		LLMC Convention 76
X	SAR Convention 79		LLMC Protocol 96
	STP Agreement 71	X	SUA Convention 88
	Space STP Protocol 73	X	SUA Protocol 88
X	IMSO Convention 76		SUA Convention 2005
X	INMARSAT OA 76		SUA Protocol 2005
	IMSO amendments 2006		SALVAGE Convention 89
	IMSO amendments 2008	X	OPRC Convention 90
X	FACILITATION Convention 65		HNS Convention 96
X	MARPOL 73/78 (Annex I/II)		OPRC/HNS 2000
X	MARPOL 73/78 (Annex III)		BUNKERS Convention 01
X	MARPOL 73/78 (Annex IV)	X	ANTI FOULING 01
X	MARPOL 73/78 (Annex V)	X	BALLASTWATER 2004

MARPOL Protocol 97 (Annex VI)	NAIROBI WRC 2007
London Convention 72	HOG KONG Convention
London Convention Protocol 96	

Description of Covered Area

Location of Tripoli Harbor

Tripoli Harbor located in the Northern area of Tripoli city (34°27'19"**N**, 35°49'14"**E**) is the second port in Lebanon after the Port of Beirut (Fig. 29). It is among the most important port on the eastern basin of the Mediterranean Sea because it is a link between East and West. The harbor covers an area of approximately 3 million m^2, with a water area of 1,500,000 m^2, and a land area that consists of 950,000 m^2, and a 550,000 m^2 of dump area destined as a future free economic zone. Indeed, Tripoli harbor is divided into two ports; the first one for harbor activities and the second for fishery activities. Harbor has 2 semi-enclosed basins due to the presence of two breakwaters 1900 m and 1300 m long respectively and 1000 m long with depths varying from 8 to 10 m for operated old quay and 1200 m long with 15.2 m depth for the new quay.

Fig. 29: Tripoli Port map.

Trade analysis

The operated quays receive general cargos and dry Bulk such as steel, wood, sugar, various kinds of beans, iron scrap, vehicles, construction material, fertilizers, coal and passengers. The new quay reserved for big ships (335 m of length) will be used for multi-purposes terminal; 400 m long specialized in the handling of containers which will start on October 2015 and the others 200 m was used in the service of dry bulk. The average of ships calling Tripoli Harbor from 2002 to 2014 is about 482 ships per year with small to medium size. The number of ships decreases during the last conflict with Israel in 2006 then increase progressively with years (Fig. 30). Moreover, the location of Tripoli harbor 80 km away from the capital Beirut and only 30 km from the border with Syria contributes in very important transit activities to Syria, Jordan, Iraq, Turkey and Gulf countries.

Logistic analysis

Import of cargoes is the predominance activity in Tripoli Harbor and the export cargoes consist mainly of scraps metals (Fig. 31). Majority of cargoes passing through Tripoli Harbor are loaded from ships to trucks for outside delivery and other parts required a storage areas within harbor. The total surface area of the warehouses and depot zones is 22375 m^2 divided on 13 warehouses of different sizes between 610 m^2 and 2752 m^2 and the open depot zones has a total surface area of 45440 m^2. In the Free zone with total surface area 150 000 m^2, there are economical and financial advantages where the goods produced and stacked in this zone are not subjected to fees and customs controls until their delivery. Cargoes operation is undertaken by a number of operators authorized from Harbor authority to carry out handling and transport operations. Table 21 shows list of equipment used during operations in Tripoli Harbor.

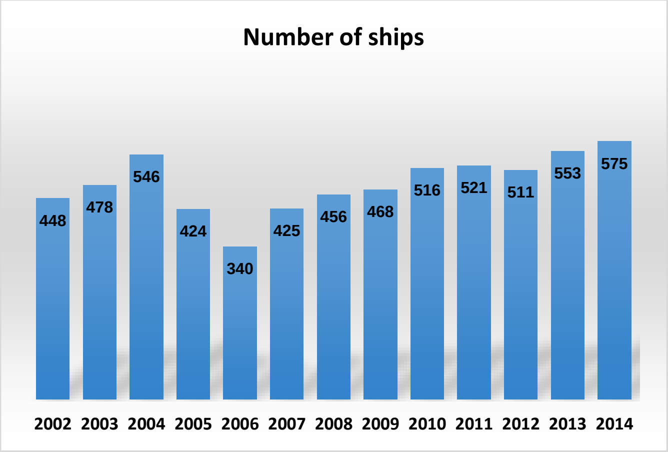


Fig. 30: Number of ships calling Tripoli Harbor from 2002 to 2014.

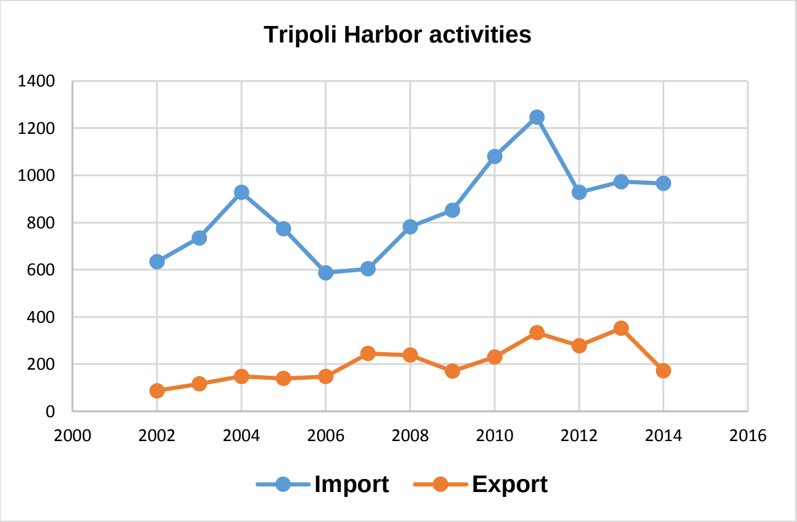


Fig. 31: Tripoli harbor activities from 2002 to 2014 in thousands of Tones.

Table 21: List of equipment used during operations in Tripoli Harbor, Lebanon.

Equipment	*Loading Capacity (Tons)*	*Number*	*Work area*
mobile cranes	50 - 160	**54**	**Present quay**
Forklifts	5 -10	**24**	**Present quay**
Top loaders for dry bulk	2 -10	**15**	**Present quay**
bulldozers	-	**8**	**Present quay**
flat and rear dump trucks	25-30	**75**	**Present quay**
Quay Gantry cranes	**-**	**3**	**Future Container Terminal**
Rubber tyred gantry cranes(RTGS) to stack containers	**-**	**9**	**Future Container Terminal**
Machines to help stack containers	**-**	**15**	**Future Container Terminal**
Machines to lift empty containers	**-**	**4**	**Future Container Terminal**
Mobile cranes	**200**	**3**	**Future quay reserved for General cargo**
Forklifts	**5 - 10**	**12**	**Future quay reserved for General cargo**
Top loaders to dry bulk cargo	**8 - 10**	**4**	**Future quay reserved for General cargo**

OEPT Contingency Planning Process

The Risk assessment will provide to the harbor authority the information on the risks faced by the port from operation incidents and pollution and can be used by harbor authority to make decisions about contingency planning (ORPC, 2015).

Risk assessment and data collection

Priority activity in the contingency planning process is to undertake a formal risk assessment of the area to be covered by this plan to assess the potential risks and hazards related to safety and pollution issues which can occurred during operations in the harbor (ABP, 2013; OPRC, 2015). Collection of data regard the vessels which visit the port in terms of number, size and frequency, the cargoes they carry, as well as any vessels which may resort to it in an emergency. And, information about harbor waters are requested during planning process such as the maximum draught which could be considered within each area – taking into account depth of water, substrate which would be encountered; the maximum length of vessel; availability of moorings, harbor tugs and piloting services; availability of containment pollution equipment; the navigational access; the local tidal / current influences; wind directions; presence of ship repair facilities and dry docks; specialist skills of the harbor workforce; the population distribution in the area under consideration and in the vicinity of harbor; presence of fishery activities within harbor; environmental issues and particular concern should giving to reserved or protected areas (bird reserves etc.) if present within or close to the area of consideration (OPRC, 2015). Majority of cargoes carried by vessels in Tripoli Harbor are in bulk which is more liable to create a safety and marine pollution incident that can be affected by the quantity, type and the number of movements of cargoes through the port. An incident either leading to safety risks or to marine pollution will be more likely during cargo handling operations than at other times. The harbor authority also should consider the potential safety and pollution hazards created by damaged and dangerous goods that may pass through the port. Both situations should be included in the risk assessment for the harbor and should cover in their plans (OPRC, 2015).

Results of the formal risk assessment

Harbor authority was taken into consideration during risk assessment process the identification of potential risks and hazards can be occurred and pollutants released from multiple anthropogenic activities in the harbor, provide an estimate of their likelihood of incidence, their probability and severity then was undertaken an assessment of their consequences. The results of this risk assessment show that we have about 8 %, 17 %, 33 %, 36 % and 6% for Negligible, Minor, Moderate, Serious and critical Risk Levels, respectively in Tripoli harbor (Table 22). The combination between the probability and consequences of an incident seems to be an effective tool during risk assessment to make a reasonable plan and will allow harbor authority to prioritize their needs for contingency planning. This classification of these hazards/Risks was based on Risk assessment Code Matrix (RAC) (Table 23).

Table 22: Results of the risk assessment performed at Tripoli Harbor.

Potential Hazards/ Risks	Types of Hazards/Risks	Probability	Severity	RF	Risk Level
The use unsafe machines, equipment and hand tools	HS	2	3	6	Moderate
Falling during construction & maintenance activities	HS	3	2	6	Moderate
Fixtures in buildings and warehouses	HS	3	1	3	Negligible
Landing a wall or ceiling	HS	2	3	6	Moderate
Falling of goods during handling operations (scraps, woods, iron, glass, etc.)	HS	3	3	9	Serious
Stand up or passing under forklifts during Handling operations	HS	4	4	16	Critical
Working at heights during handling operations	HS	4	2	8	Serious
Vehicle accidents	HS	2	3	6	Moderate
Slips, Trips and Falls on the floor, on stairs or in water	HS	3	3	9	Serious
Confined spaces	HS	2	2	4	Minor
Noise and Vibration emissions from generators	HE	4	2	8	Serious
Electricity	HS	2	3	6	Moderate
Use of gas machinery, presence of gas bottles or gas leakage.	HS	2	4	8	Serious
Fire accidents	HSE	2	4	8	Serious
Exposure to hazardous chemicals (pesticides and coal)	HSE	4	3	12	Critical
Dust emissions during handling operations of bulk cargoes and scraps	HSE	3	2	6	Moderate
Radiation from some good (scraps)	HS	2	3	6	Moderate
Gas emissions from machinery, equipment, vessels, vehicles and generators)	HE	4	2	8	Serious
Exposure to chemical pollutants from dredging materials (Heavy metals, Persistent Organic Pollutants…)	HE	1	2	2	Negligible
Exposure to oil residues released from ships (bilge water) and machinery/equipment	HSE	2	3	6	Moderate
Increase of relative humidity in warehouses	HS	4	2	8	Serious

Oil spills accidents	HSE	2	4	8	Serious
Vessels shipwreck	HSE	1	4	4	Minor
Solid waste from vessels offices, warehouses, operations and fishery activities	HE	3	3	9	Serious
Presence of Sewage outfalls	HE	4	4	16	Critical
Ships discharges (sewage & Ballast)	HE	2	3	6	Moderate
Slaughterhouse effluent	HE	3	3	9	Serious
Lixiviate from dumping site	HE	3	2	6	Moderate
Surface water Runoff	E	3	2	6	Moderate
Noise	HE	4	2	8	Serious
Hard work	H	2	3	6	Moderate
Computer user’s for long time	H	3	3	9	Serious
Non comfortable furniture	HS	2	2	4	Minor
Routine work	H	4	1	4	Minor
Restricted spaces	HS	1	1	1	Negligible
Working at heights at offices	HS	2	2	4	Minor
Tsunami and earthquake	HSE	1	4	4	Minor

*H: Health, S: Safety and E: Environmental Hazards/ Risks.

*RF: Risk Factor

* Colored rows in grey related to hazards and risks included in contingency plan for this time.

Indeed, this risk assessment will be subjected to regularly sensitive analysis and updates to avoid uncertainties and to identify where results are particularly sensitive to changed assumptions. If not, the use of results may lead to some highly spurious outcomes. Risk assessment is therefore a continuous process in practice. The results of this sensitive analysis give harbor authorities an insight into the level of confidence they can apply to decisions on contingency planning. Moreover, for an effective analysis these results need to be shared with others to realize the mutual benefits and establish mutual support arrangements help harbor authority in contingency planning process in particular during the implementation phase. Some examples of local authorities who involved in the contingency planning are Ministry of Public Works and Transport, Ministry of Environment, General Directorate of Land and Maritime Transport, Harbor Master, Council of Development and Reconstruction (CDR), Urban Community AL- FAYHAA (Union of three municipalities), Maritime Army, neighboring ports as the case of fishery port and consulters who can advise on whether the consequences have been adequately assessed.

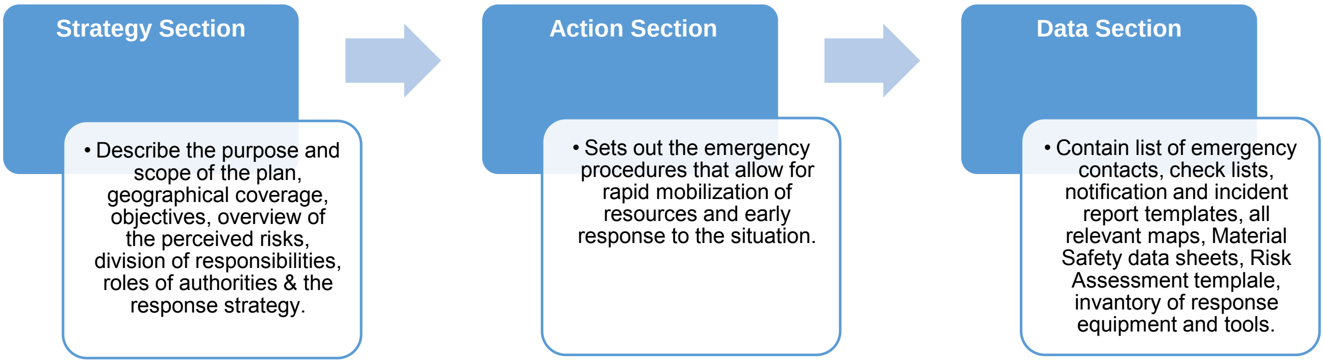
Table 23: Risk assessment Code Matrix (RAC).

	Probability			
Consequences	**Frequent (4)** Immediate danger to health and safety of the public, staff or property and resources.	**Likely (3)** Probably will occur in time if not corrected, or probably will occur one or more times.	**Occasional (2)** Possible to occur in time if not corrected	**Rarely (1)** Unlikely to occur; may assume exposure, will not occur.
Catastrophic (4) Imminent and immediate danger of death or permanent disability.	**16** **CRITICAL**	**12**	**8**	**4**
Critical (3) Permanent partial disability, temporary total disability	**12**	**9** **SERIOUS**	**6**	**3**
Significant (2) Hospitalized minor injury, reversible illness	**8**	**6** **MODERATE**	**4** **MINOR**	**2**
Minor (1) First aid or minor medical treatment	**4**	**3**	**2**	**1** **NEGLIGIBLE**

Description of Management Plans

Structure

Indeed, Contingency Plan is a part of ISO 14001 and 18001 management systems which include plans and procedures should be prepared following to the structure described in Fig. 32 (ABP, 2013; OPRC, 2015).



Strategy Section

- Describe the purpose and scope of the plan, geographical coverage, objectives, overview of the perceived risks, division of responsibilities, roles of authorities & the response strategy.

Action Section

- Sets out the emergency procedures that allow for rapid mobilization of resources and early response to the situation.

Data Section

- Contain list of emergency contacts, check lists, notification and incident report templates, all relevant maps, Material Safety data sheets, Risk Assessment template, invantory of response equipment and tools.

Fig. 32: Structure of Contingency Plan.

OEPT Fire Safety Management Plan (OEPT/FSMP)

Indeed, OEPT harbor authority give a great concern for fires accident due to a serious fire accident was occurred at Tripoli Harbor in august 2014. Moreover, the results of risk assessment show that fire Hazards were classified as serious hazards at Tripoli Harbor. Therefore, a contract was made with a consultant company for the elaboration of OEPT Safety Code Practice includes a fire safety management plan will support OEPT contingency Plan prepared and managed with the collaboration between harbor authorities, Health, Safety and Environment Department (HSED), and involved parties. This Safety code includes some suggestions and instructions help and assist harbor authority to manage and response any fire incidents may can occur in harbor. The main issues proposed in this code are (OEPT, 2015 a, b):

- Prepare a Fire Policy
- Carry out a fire risk assessment for all buildings, warehouses, piers, working and open storage areas.
- Creation an Emergency Room (ER) and Emergency response Team (ERT)
- Ensure that all ERT staff members are proper qualified and receive fire safety training at regular interval.
- Undergoing a training sessions for employees to familiarize with the use extinguisher.
- Carry out a fire drills (one fire drill per annum minimum).
- Instructions concerning the storage of Hazardous and dangerous substances.
- Safe practices in warehouses.
- Instructions concerning Rescue and Evacuation Plan.
- Fire Response strategy.
- Inventory of required firefighting equipment and periodical checks.
- Instructions during bunkering operations.
- Preventive measures to avoid the spreading of fires and explosion.

This safety code was reviewed by HSED and then sent to Tripoli harbor authority for approval. Table 24 summarized the flowchart of OEPT Fire response strategy (OEPT, 2015b). Indeed, Harbor authority will use its own resources to response for incidents arise from routine operations, such as fires by providing extinguishers in all offices and public warehouses, fire truck and water feeding stations at designated locations and will share this code safety practices with all contractors and leaseholders in order to implement the requested instructions in particular that related to the installation of automatic fire-extinguishing systems and warning fire signs throughout the warehouses. Also, will integrate a new application request tendered to store dangerous goods in harbor warehouses' subjected to restricted conditions during handling, labeling, transportation and storage operations to comply with the international Maritime Dangerous Goods Code' (IMDG) published by the IMO (OEPT, 2015a). Also, a great concern will be paid also by HSED for the implementation of the requested preventive measures by conducting a frequent safety conditions checks in order to distinguish fires at initial stage and avoiding ignition sources. Only then will the effectiveness of this code safety practices can be ensured.

OEPT Fire Response Strategy

Table 24: Table 24 OEPT Fire Response Plan.

Nº	*Flow Chart*	***Persons of charge tasks:***
1	**Discovering & Notification Fire**	1. Raise fire alarm if available 2. Call OEPT Emergency Room (OEPT/ER) 3. Notice all colleagues and visitors 4. Tackle fire with nearest fire extinguisher without risk or proceed to exit area 5. Switch off Electricity 6. Provide useful information for ER
2	**OEPT Emergency Room supervisor (OEPT/ERS)**	1. Call Port Manager 2. Call HSE Department (HSED) 3. Call Emergency Response Team members (ERT) 4. Call National Fire Department (175) 5. Call Red Cross (140) 6. Call Harbor Electrician 7. Alert Security office, Harbor Master, Military, Police… 8. Proceed to fire location to assess Severity of incident 9. Advise ERT of any special risks (e.g. flammable materials…) 10. Submit a Written report to HSED giving full details about incident
3	***Emergency Response Team (ERT)***	1. Review map of the location 2. Aware about exit routes 3. Provide yellow vest for all involved in response actions 4. Activate rescue and evacuation plan of all Personal (with special need if present) 5. Ensure all peoples evacuate to assembly Point and do not leave it 6. Ensure that all evacuation action are competed 7. Activate firefighting response strategy following to Fire response procedure 8. Start firefighting response using harbor equipment (fire extinguisher, ABC Dry powder and fire truck…) 9. Guide firemen to proceed to water feeding stations 10. Arrange first aid 11. Fill all related checklists 12. Submit a written report about observations and comments to HSED.
4	***HSED***	1. Direct all operations on field by cooperation with ERT 2. Manage communication between all concerned parties 3. Conduct impact assessment after incident for peoples, locations, goods and equipment 4. Evaluate loss of property and work time 5. Management of fire waste

		6. Supervise the maintenance operations of fire safety precautions (tools and equipment) 7. Collect and record all Checklists and Reports 8. Evaluate Rescue and evacuation Plan and 9. Evaluate Fire Response Plan and procedure 10. Incident reporting, investigation and analysis procedures (Fig. 33) 11. Review formal risk assessment and OEPT contingency plan for any modifications 12. Submit written report to Port Manager with recommendations.
5	***Harbor Authority***	1. Review submitted report 2. Approve recommendations (corrective and preventive actions) suggested by HSED 3. Approve the updated version of risk assessment and contingency plan 4. Media release

After each incident, HSED should follow the Incident reporting, investigation and analysis procedures included in the management system ISO 18001 (Fig. 33).

<table>
<tr><td rowspan="3"></td><td rowspan="3">PORT OF TRIPOLI
Ministry of Public Works and Transportation
Oil Spill Emergency Response Plan</td><td colspan="3">ISSUE DATE: January 2013</td></tr>
<tr><td>Volume
28</td><td>Chapter
2</td><td>Version
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Incident Investigation Flow Chart

Fig. 33: Incident investigation Flow Chart.

Oil Spill Emergency Response Plan

Oil risk assessment and data collection

The first thing to be done when planning a process is to conduct a risk assessment in order to provide all of the information that can be used for the contingency planning (ABP, 2013; OPRC, 2015). Tripoli harbor does not service any liquid bulk hydrocarbon trade. Results of data collection regarding vessels which visit the port in terms of number, size, the cargoes they carry, water depth, and maximum length of vessel. Also, other information concerning tidal regime, wind’s speed and direction, availability of containment tools and tug boat, and the presence of the natural reserve within or close the harbor were taken in consideration during assessment. On the other hand, we have a great lack of data concerning water pollution. Therefore, Health, Safety & Environment department (HSED) conducted an assessment to water and sediment pollution (Merhaby et al., 2015) and will prepare a survey for vessels and bunkering companies in order to create a data base useful in this risk assessment. However, it is estimated that four to five oil spill accidents occurred last year in OEPT basins. These incidents were classified as serious hazards in the formal risk assessment included in ISO 14001 & 18001 management system. Indeed, the risk assessment is a continuous process and will be regularly analyzed and updated to avoid uncertainties.

OEPT Oil Spill Emergency Response Plan

Plan Description

This plan is provided to assist the OEPT Authority and the Harbor Master. It includes details of contingency arrangements for responding to actual or threatened oil pollution incidents that may occur in Tripoli harbor basins. Its primary purpose is to identify all credible scenarios, outline the responsibilities and set in motion the necessary actions in a structured, logical and rapid manner to stop or minimize the discharge and/or to mitigate its effects. This response plan is designed to deal with small (Tier One) and medium (Tier Two) oil spillages. Harbor Master is responsible to conduct oil spill response operations within the Port and will be supported by Emergency Response Team (ERT) created by the harbor. Depending on the circumstances of the incident, ERT will be involved using its own resources. In this case, ERT will provide the command and control structure to coordinate and direct the response. ERT under the chairmanship of the Harbor Master, will be established at the Port Marine Response Centre and it consists of representatives from the following organizations and authorities: Harbor authority (Port Manager), Technical Department (Engineers and technicians), HSED (Environmental and safety officer), Harbor Security officer (Captain), representative from General directorate of Land and Maritime Transport (Marine Manager) and consultant from Maritime Safety Company. Other parties can also be added such as a vessel owner or a representative from shipping agency, from Coast guards, maritime police, army and Corus (if appropriate) for Tier Two incidents.

Once oil spilling is detected in harbor waters ERT, Captains or vessel masters, port users, and oil companies (bunkering) should immediately report to the Harbor Master. Action sheets that follow a methodical checklist style to effectively guide the Harbor Master, ERT and harbor manager through the actions that they will be expected to take will be provided. The list of their responsibilities are also included in Strategy Section of the plan. Moreover, the data section includes a list of emergency phone numbers; a list of alternative telephone and facsimile numbers is also included in Data Section. The communications between Harbor Master, Marine Response Centre with external authorities and organizations will be undertaken by telephone and facsimile. Communications between the Harbor Master, the Marine Response Centre and harbor personnel engaged in the response to small oil spill incident will be primarily done via wireless devices (private channel) and mobile phones. After each oil spill incidents, number of checklists should be filled by the people involved in the incident response that are summarized in Table 25. And, HSED should follow the Incident reporting, investigation and analytical procedures included in the ISO 14001 & 18001 management system to investigate the cause of the incident and submit the incident report.

Table 25: Lists of Checklists included in the Oil spill emergency plan.

Checklists	***Description***
Oil Spill Incident Checklists	Intended to promote consistency of approach by all personnel involved in the incident response.
Oil Spill Assessment Checklist (OSAC)	Ensures that the initial assessment of the oil spill is accurate and all aspects likely to affect the classification such as quantity, oil type and likely fate of the spilled oil, are investigated.
Incident Briefing Checklist (IBC)	Ensures that all personnel involved in the management of the incident are given a thorough briefing, and are then able to give a consistent and effective briefing to personnel under their control during the incident.
Personal Log Checklist (PLC)	Ensures that all personnel involved in the incident response record correct and relevant information throughout the operation; consistent logs and records can then be submitted to the Harbor Master and HSED for his use in subsequent reports and actions.
Oil Spill Sampling Checklist (OSSC)	Ensures that samples of sufficient quantity will be taken, sealed, labeled and handled correctly.

Response strategy

The response strategy has been developed taking into account the spill risks and possible sources of spillage associated with the port operations, including oil spills or oil that is intentionally released from vessels and bunkering operations (Fig. 34). The key steps in the response strategy are to do an immediate assessment that allows a rapid response. Some factors that affect the response actions within Harbor basins like tidal regime, wind speed and direction should be available at the time of the incident. The primary response to Tier One incidents in OEPT will be by the use of its own resources such as a Tug boat, Oil spill eater, Troilboom AFPU750 with its related accessories and materials. An assembly of suitable equipment and their locations is included in the Data section. The Response strategy that is described in figure 34 covers the two oil types Light and Heavy Oil. In addition, the Action Section of the plan includes also health and safety guidelines for all of those involved in oil spill response activities including Safety Plan Assessment Form. Other information like site characteristics, site hazards, the available protective equipment and site facilities are also included to ensure that all health and safety requirements are considered for appropriate actions to be taken under the supervision of HSED. Moreover, Waste management plan is a necessity as oily waste is classified as Hazardous Waste and the transfer and disposal of such materials are subjected to elevated restrictions. Whenever possible, spilled oil should be recovered for recycling and re-usage. In this plan, waste management and Temporary Storage/Clean, Treat, Stabilize, Recover, Reuse is proposed since it is the best practical environmental option (BPEO). For, Tier One and Tier Two incidents oily wastes will be transferred to the waste oil disposal/recycling contractors. However, the Harbor Authority and HSED must confirm that any contractors have the needed license to handle and dispose the waste. A Training and Exercise Policy was provided in this plan to ensure that those involved in the response to oil spill incidents will undergo periodic training including notification, mobilization and incident management exercises in order to react quickly to any oil spill incident. The Data section also includes templates for Oil spill progress report, Contractor report, results of samples analysis, Product ingredient sheets (MSDS), roles and responsibilities of every individual involved in the plan, risk assessment results and information about the natural reserve islands (Palm, Sanani and Ramkin) located at 5.5 Km from the coast which may face important threat in case of Tier two oil spill incident.

Finally, the effective management of any incident is based on four fundamental elements: the quick response of the organization with functional teams, the assigning of specific roles and responsibilities for involved personnel, the availability of internal and external communication system, providing the suitable resources and the use of modern technology by well-trained personnel. Moreover, this plan needs to be shared with local authorities who are involved in the contingency planning to realize the mutual benefits and establish mutual support arrangements. Some local examples are Ministry of Public Labor and Transport, Ministry of Environment, General Directorate of Land and Maritime Transport, Harbor Master, Maritime Army, neighboring ports as the case of fishing port and consulters who can advise on whether the consequences have been adequately assessed. Only then will the effectiveness of this plan can be ensured.

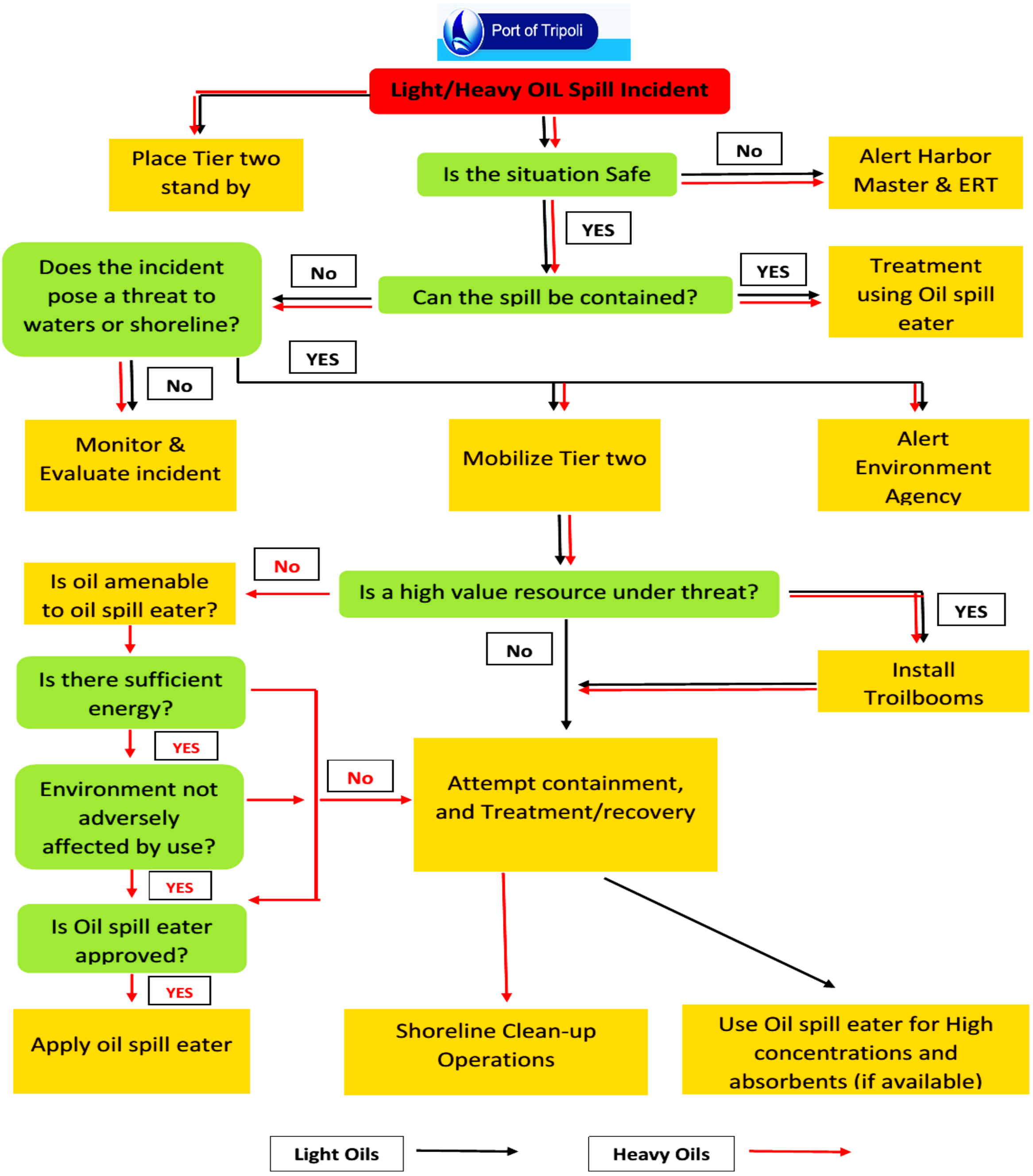

Fig. 34: Light and heavy Oils spill response strategy.

Conclusion

The durable development is not an easy matter. Every company or organization should to take into consideration the balance between its three fundamental elements economic, social and environment aspects to reach their objectives. Therefore, the contingency plan can be considered valuable tools will help and assist Harbor authorities to improve the safety for those who use or work in harbor, their ships, passengers and cargoes, and the environment. OEPT Contingency Plan is consisted from multiple plans are: the Fire response Plan, Oil spills Response Plan and Waste Management Plan should be complete in the near future. Will facilitate and guide the response to any emergency or incident within the OEPT Port limits and to comply with national and international obligations. These plans, which harbor authorities have adopted and agreed to implement, proposed that all the functions of a harbor authority and concerned parties in relation to port operations should be regulated through a safety management and communication systems, based on a formal risk assessment of the hazards facing their port, appropriate response strategies and measures in order to prevent or minimize their potential environmental and economic damage by using its own resources. During planning process some considerations should be taken into consideration such as Consultation with statutory authorities and concerned parties, Collect and sharing necessary Information and to make partnership approach in order to avoid any gaps in the contingency plan. To ensure the effectiveness of these plans harbor authority should to familiar with key response functions, conduct a regularly exercised and reviewed and updated it on a regular basis. These plans were elaborated for long term (Five years) and their best implementation will ensure the durable development in Tripoli Harbor. In parallel, an environmental assessment for organic and inorganic pollutants in sediments of Tripoli harbor was conducted in order to fill the great gaps of information in the risk assessment and the results will help harbor authority to identify the main sources of water pollution in order to take the appropriate mitigations measures. For the benefit of other harbor authorities these plans will be provided soon in the official website of Tripoli Harbor: www.oept.gov.lb.

Acknowledgment

Authors would thank Eng. Abdelrahman HAJAR, Head of Technical Department, Captain Abdulkader Issa and Dr. Sopheak NET for their continuous support and fruitful advices.

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CONCLUSION ET PERSPECTIVES

L'augmentation des activités anthropiques qui se concentrent principalement dans les zones côtières, permettant par conséquence la libération d'un très grand nombre de polluants organiques et inorganiques persistants dans l'environnement, contribuent significativement à la modification de l'écosystème. Les polluants organiques et les métaux lourds sont connus comme toxiques, persistants, bioaccumulatives et s'accumulent dans les matrices environnementales biotiques et abiotiques. Ces polluants sont adsorbés préférentiellement sur les particules, les mécanismes d'interactions sont influencés par la température, la surface et la taille des particules et les conditions géochimiques du milieu (e.g. la salinité, la turbidité et les conditions d'oxydoréduction). Dans l'écosystème marin, les sédiments sont considérés comme un réservoir mais également comme source de ces polluants pour la colonne d'eau. Beaucoup de mécanismes favorisent la remobilisation et l'oxydation de sédiments provoquant la désorption des polluants et par conséquent leur accumulation dans les phytoplanctons et les organismes aquatiques qui entrent dans chaîne alimentaire. Leurs propriétés cancérigènes et mutagènes provoquent également une grande menace pour la santé publique. Pour ces raisons, les études de la qualité des sédiments sont largement utilisées comme un outil pour connaître le niveau de contamination de l'eau et d'évaluer le risque écologique potentiel sur les écosystèmes.

Malgré tous les efforts internationaux réalisés au cours des programmes de suivi, il y a encore un manque d'information sur certains polluants et zones géographiques. Notre étude sur la distribution de la concentrations de certain POPs dans les sédiments (HAPs et PCBs) montre que 75% des études se concentrent principalement dans les pays industrialisés et urbanisés situés dans la partie nord-ouest et sud-ouest de la Méditerranée qui ont les ressources techniques et financières appropriées pour répondre à ces besoins et de réagir contre la pollution, tandis que la partie est et sud sont moins étudiées à l'exception de la côte égyptienne et récemment la côte libanaise. Ce qui indique que le niveau socio-économique entre les pays est à l'origine de cette lacune d'information. Cette étude menée sur le bassin méditerranéen donne une vision globale sur le niveau de contamination. Les résultats indiquent la présence de plusieurs zones chaudes dans ce bassin. L'Italie, la France, l'Espagne, l'Egypte et la Turquie sont les principaux pays qui contribuent à la pollution de la Mer Méditerranée par les HAPs et les PCBs. Une contamination plus importante des sédiments par les composés cibles se trouvent dans les zones côtières des grandes villes en raison des degrés d'industrialisation et d'urbanisation croissante. Des niveaux de contamination relativement élevés ont été détectés dans les échantillons des sédiments prélevés dans les baies, les ports, les lagunes et les estuaires. On constate que la Mer Méditerranée est dans une situation critique, la question qui se pose donc que sera la situation après dix ou vingt ans ?.

Dans le bassin oriental de la Méditerranée, le Liban a signé la convention de Barcelone, mais jusqu'à aujourd'hui il n'y a pas assez de progrès dans le domaine de l'environnement au niveau local ou gouvernemental. Même si le Liban n'est pas un pays industrialisé, il souffre de la mauvaise gestion des aspects environnementaux qui provoquent la dégradation de l'écosystème. Dans son cas, la coopération entre les entreprises et les centres de recherche est une solution efficace pour répondre à ces exigences. Notre travail est une des premières études sur le Liban qui prend en considération en même temps la pollution organique et inorganique dans les sédiments de la côte libanaise. Une attention particulière a été prise pour les zones portuaires et les baies en raison de l'hydrodynamisme et l'échange d'eau limitée qui les rend plus vulnérables à l'accumulation de ces polluants. Au Liban, la contamination des sédiments marins par les HAPs, PCBs et métaux lourds indiquent la présence de plusieurs points chauds à proximité des grandes villes, qui sont significativement affectées par les zones industrielles, portuaires et les apports fluviaux. Le Port de Beyrouth présente les plus hauts niveaux de pollution au Liban tandis que les chaînes de montagnes jouent un rôle de piège pour certains contaminants dans autres régions comme dans le cas de la baie de Chekka.

La pollution par les HAP et PCB est considérée comme modérée pour tous les sites d'échantillonnages du Liban à l'exception au Port de Beyrouth qui est fortement pollué. La combustion est la source prédominante dans la majorité des stations ainsi que le stockage du charbon contribue fortement à cette pollution comme c'est le cas au port de Tripoli. Les dépôts atmosphériques sont la source principale de la pollution des sédiments par les PCB. Les effets écotoxicologiques sont possibles pour la majorité des stations le long du littoral libanais.

Ainsi que pour la contamination par les éléments traces métalliques, le Port de Beyrouth présente les plus hauts niveaux de pollution due à la contribution significative du Zn et Pb. Les pourcentages de mobilités sont plus que 50 % pour la majorité de ces éléments à l'exception du Pb qui sont considérés moins mobiles. Les concentrations des cinq éléments traces métalliques (Cd, Zn, Pb, Cr and Co) sont trouvées à des niveaux supérieurs aux valeurs de références déterminés pour la croute terrestre dans les sédiments du Port de Beyrouth, Port de Tripoli, la baie de jouniyeh et l'estuaire de la rivière Abou Ali. Le facteur d'enrichissement (FE) indique que les activités anthropiques contribuent significativement à la pollution des sédiments côtiers par le Cd, Pb et Cr particulièrement au Port de Beyrouth qui est classé comme le site le plus pollué. Au Port de Tripoli, la contamination est considérée comme modérée due aux activités de transport maritime, d'entretien des navires et les rejets urbains. L'effet biologique négative reliée aux métaux Cd, Pb and Zn est estimé comme fréquent dans le Port de Beyrouth sur la base du critère de qualité des sédiments (SQGs) alors que pour le Port de Tripoli est considéré comme occasionnel pour les stations proches des activitées de maintenance des navires et des rejets des eaux usées. L'affinité importante de ces polluants à la matière organiques rend les méthodes de remédiations trop chères et inefficaces, l'élimination à la source est une stratégie plus efficace. Les résultats de ce travail peuvent être utilisés comme une base de données pour stimuler le gouvernement et les autorités locales à préparer des stratégies, les politiques et les programmes d’action pour une meilleure gestion de la qualité de l’eau, des sédiments et de la biodiversité. La notion de gestion de l’environnement doit être intégrée dans de développement économique le long du littorale Libanais surtout avant de mise en œuvre les activités prévues et reliées au secteur de l’exploitation de gaz et du pétrole. En plus, encourager l’autorité des deux principaux ports au Liban à prendre l’initiative pour caractériser le niveau de pollution dans leur basins afin d’identifier les sources majeurs et prendre les mesures de contrôles ou d’éliminations nécessaires pour de lutter contre la dégradation de l'environnement. Il est donc recommandé de réaliser une étude détaillée sur le site du Port de Beyrouth. Des études de suivis permanant sont recommandés pour ces sites d’études et pour d’autres sites possibles d’être pollué ou sensibles le long du littorale libanais comme l’île des Palms.

Des études futures concernant la contamination historiques des sediments par carottage, la biodisponibilité de ces polluants dans les sédiments, leurs concentrations dans la phase dissoutes et particulaires dans l’eau et des études toxicologiques sur des organismes aquatiques sont encore à recommander afin d’établir une image claire et globale de la pollution dans ces sites. Des activités de sensibilisation pour les utilisateurs du littoral, des pêcheurs et du public concernant ces types de polluants sont désormais importantes. L’embauche des spécialistes dans le domaine de l’environnement dans les industries et les Ports est nécessaire afin de développer les stratégies et les politiques de contrôle et de suivi environnemental; en créant un système de communication entre les industries, les autorités locales et les centres de recherches. La participation dans des projets régionaux et internationaux est considérée comme un des outils efficaces pour améliorer les capacités des institutions et des industries et créer un système de communication assez important pour l’échange des informations, les expériences et une meilleure pratique comme par exemple l'expérience du Port de Tripoli dans le projet MESP (Management Environnemental dans les Ports pour un développement durable), qui lui a permis de prendre certaines mesures pour réagir contre les accidents du déversement des huiles dans ses bassins et établir un laboratoire pour le suivi de la qualité de l’air, de l’eau et du bruit dans le Port.

CONCLUSIONS AND PROSPECTS

The increasing pressure of anthropogenic activities which concentrate mainly in the coastal areas allowing the release of a very large number of organic and inorganic persistent pollutants in the environment leading subsequently to a significant modification of the ecosystem. Due to the physicochemical characteristics, POPs and Heavy metals are known as a toxic, persistent, bioaccumulative and disposed to a long range transport in the environment enable them to reach areas as far as from their emission sources and accumulate in biotic and abiotic environmental matrices. In the environment these pollutants are preferentially absorbed by particles then transported by multiple pathways including dry and wet atmospheric deposition and air-water surface exchange and they are subjected to fractioning and partitioning processes mainly influenced by the effect of surface and particle size, ambient temperature and geochemical gradients (e.g., salinity, turbidity and redox conditions).

In marine ecosystem, the sediment is not considered only as final reservoir of these pollutants but also a sink and source to water column and atmosphere. Many mechanisms enhanced sediment remobilization and oxidation leading to the desorption of these pollutant and their return to water column to join the re-cycling environmental processes by volatilization and accumulate in phytoplankton and aquatic organisms up to food chain. Their carcinogenic and mutagenic properties causing also a great threat to public health. The toxicity of trace metals take more concern since the reason that they are not removed from water and sediments by self-purification. Wherefore, sediments quality is widely used as a tool to understand current water pollution and assess their potential ecological risk in coastal ecosystems.

Although, the international efforts done during MED POL program regarding monitoring activities we still have a lack of information about for certain pollutants and geographical areas. Our survey about the distribution of some POPs concentrations in sediments (PAHs and PCBs) shows that 75 % of these studies concentrate mainly in the industrialized and urbanized countries located in the northwestern and southwestern part of Mediterranean Sea which have the appropriate technical and financial resources to meet these needs and react against pollution while the eastern and southeastern part is neglected with the exception of the Egyptian coast and recently Lebanese coast. Indicating that the socio-economic pattern between countries is the cause of these gaps of information. This survey conducted in our review on Mediterranean region make easier to perform a similar study at global scale on the future. As results we observed numerous hotspots sites in Mediterranean countries. Italy, France, Spain, Egypt and Turkey are the main Mediterranean countries contributed to PAHs and PCBs pollution in the 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 which are mostly concentrated in

NWE, TYR, ADR, AEG and SLE (Egyptian coast) Sea. Relatively high contamination levels were detected in sediments samples collected from bays, harbors, lagoons and river mouths. Although, the technical and analytical development we have also a great lack in information 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 so the question is what will be the situation after ten or twenty years?.

In the eastern basin of Mediterranean Sea, Lebanon has ratified the Barcelone convention but until today there isn't any progress in this field at governance or local level. Even that is not an industrialized country, but they suffer from the mismanagement of the environmental aspects, which cause the degradation of the ecosystem. In this case the cooperation between companies and research centers is an effective solution to meet these requirements. Our work is the first study on Lebanon coast, which takes into consideration the organic and inorganic pollution in sediment. A particular concern was taken to harbors and bays areas due to the scare hydrodynamism and limited water exchange, which make them more vulnerable to the accumulation of these pollutants. In Lebanon, the contamination of the marine sediments by PAHs, PCBs and heavy metals indicating the presence of hot pollution levels in coastal sediments of big cities significantly affected by industries, harbor activities and riverine inputs.

The assessment study of organic contamination in coastal surface sediments of Lebanese coast show that the highest contamination of PAHs, Me-PAHs and PCBs were localized at Port of Beirut, which is located in densely populated area and subjected to multidisciplinary activities including industrial inputs, intensive shipping and transport activities whereas high trees of mountain regions play as a trap of these contaminants at Chekka bay. Tripoli Port was found moderately to highly polluted with PAHs and the biological adverse effects were expected to occur occasionally for fishery basin and old basin of harbor. Pyrogenic process was found the predominance source in the majority of stations and the coal dust contributes primarily in this pollution at Port of Tripoli. The atmospheric deposition is the primarily source of PCBs in coastal sediments. For PCB contamination the biological adverse effects were expected occasionally for the majority of studied stations along Lebanese coast.

For the inorganic assessment study show that Port of Beirut was found the most polluted site with the significant contribution of Zn and Pb in this metal contamination. The percentage of mobility of almost all trace metals in sediments of studies stations is up to 50% except for Pb, which were found the less mobile trace metals. The concentrations of five trace metals (Cd, Zn, Pb, Cr and Co) were found exceeded the background values at four sites; Port of Beirut, Port of Tripoli, Jounieh Bay and Abou Ali estuary. The enrichment factor (EF) is considered as an effective tool to differentiate between the natural and anthropogenic sources indicating that the anthropogenic activities contribute significantly to the coastal sediment pollution with Cd, Pb, Zn and Cr particularly at Port of Beirut, which is classified as highly polluted site. At Port of Tripoli, metal contamination was classified as moderately indicating that the harbor basin was significantly affected by handling and shipping activities, shipyards area and sewage outfall. According to the SQGs, the biological adverse effect of Cd, Pb and Zn were expected to occur frequently at Port of Beirut whereas at Port of Tripoli were expected to occur occasionally for the samples collected from the corner of old basin, close to ship maintenance areas and sewage outfall.

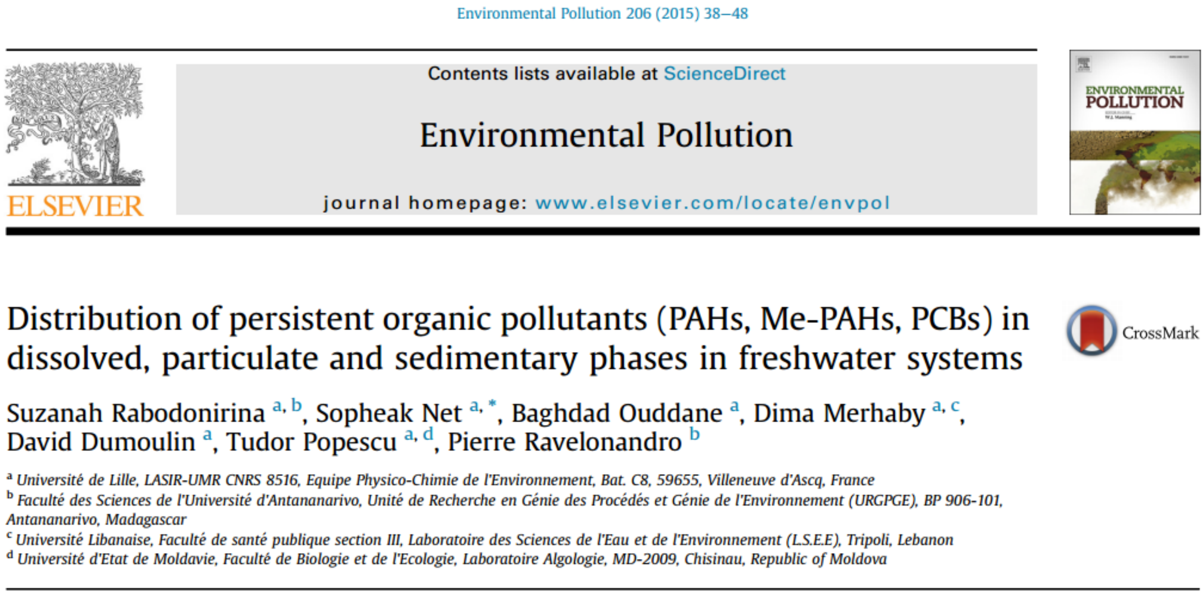
The high affinity of these organic and inorganic pollutants to organic materials makes the remedial actions very expensive and insignificant so the proper treatment of industrial effluents and municipal wastewaters is a better strategy to control the sediment pollution in harbors by reducing the released of these pollutants at the source. The results obtained from this thesis would be helpful in developing more effective harbor management strategies to control and monitor the pollutants discharges into Tripoli Harbor basins and detailed study is recommended to Port of Beirut in order to take the suitable decisions and adopt an adequate pollution control strategies. Therefore, these results should be used to stimulate the governance, local authorities to carry out some strategies, policies and programs of integrated coastal zone management on biodiversity, sediment-water quality and economic activities along Lebanese coast in particular before starting the future activities in gas and oil sector. In addition, stimulate the Ports authorities of these two main ports in Lebanon to take the initiative and start the investigation about the level of pollution in their basins.

A continuous monitoring of sediment and water quality was recommended at all studied stations and others possible hotspot or sensitive areas along LCZ such as Palm Island. And, future studies are needed concerning the historic contamination of core sediments by these pollutants, their bioavailability and toxicological studies on aquatic organisms in order to have a clear picture of Lebanese coast pollution. The publication of the results is a necessity for the overall benefit. Sensibilization campaigns for users, fisherman and public from local authorities are requested to increase the awareness regard this types of pollution. The employment of environmental specialists in industries and harbors for developing strategies and policies for pollution control and research through the cooperation with research center and local authorities, or creation a proper research center inside the companies can be the first steps to ensure environment sustainability towards a durable development. The participation in regional and international projects can be considered also as an effective tools to assist the capacities of institutions and industries by creation an important communication network for information, experiences and best practices exchange such as the experience of Tripoli harbor in MESP project (Managing the sustainability in Port for a durable development) which was support and assist the Port authority to take some mitigation measures regarding oil spills into its basins and establish a laboratory in order to continue the monitoring activities of air, water and noise quality inside the Port.

APPENDIX

Article 1

Distribution of persistent organic pollutants (PAHs, Me-PAHs, PCBs) in dissolved, particulate and sedimentary phases in freshwater systems.



Environmental Pollution 206 (2015) 38–48

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Distribution of persistent organic pollutants (PAHs, Me-PAHs, PCBs) in dissolved, particulate and sedimentary phases in freshwater systems

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Abstract

The occurrence of three groups of hazardous organic contaminants (PCBs, PAHs, Me-PAHs) in fifteen watercourses and rivers located in highly urbanized and industrialized zones was studied. The distribution of 62 organic contaminants was determined in three matrices: in the dissolved phase, associated with suspended solid matter (SSM) and in sediment. Their distributions in the aquatic environment depend strongly on their physicochemical properties. Low molecular weight PAHs were predominant in the dissolved phase while those with high molecular weight accumulated preferentially in SSM and sediments. Among the 28 PCBs congeners, only PCB153 was detected. The results showed that the contamination of these areas originated mainly from combustion processes. The three the most polluted sites identified are surrounded by big cities. Ecotoxicological assessment based on the international Sediment Quality Guidelines (SQGs) showed that the toxic effects of the sediment in these watercourses and rivers occurred due to high levels of hydrocarbons.

Keywords: POPs, sediment quality, water column, The Scheldt, Ecotoxicological risk.

1. Introduction

Aquatic environments in industrialized countries are frequently exposed to numerous toxic organic pollutants generated by various discharges. Watercourses and rivers constantly reveive various kinds of organic contaminants from municipal, hospital and industrial wastewaters, agricultural effluents and nonpoint source pollution. To date, various watercourses, lakes, rivers, estuaries and seas have been contaminated by a wide range of organic substances including the persistent organic pollutants (POPs) (Boonyatumanond et al., 2006; Merhaby et al., 2015; Net et al., 2014a, 2014b, 2015a, b, c). Polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are toxic and persistent in the environment. Due to their hydrophobicity, they tend to accumulate in solid matrices and in fatty tissues of organisms rather than entering in aqueous dissolved phase (Wenning and Martello, 2013). They have been detected in sediments and in many aquatic species such as marine algae, invertebrates, fishes, dolphins and many other aquatic organisms (Arias et al., 2015a, b; Gui et al., 2014; Net et al., 2015a, b).

PAHs and Me-PAHs can be originated both from natural processes and anthropogenic inputs (Lu et al., 2012). Anthropogenic origins are generally the major sources of PAHs pollution in the environment (Yunker et al., 2002). PCBs were used in industry as heat exchange fluids, in electric transformers and capacitors, and as additives in paint, carbonless copy paper, and plastics (UNEP, 2008). Industries contributed for a large amount of PCBs into aquatic environment by their improper disposal (Özyürek et al., 2013). Even though their production has been banned since 1979 (US-EPA, 2013), PCBs are still present in the environment (Bigus et al., 2014; Dumoulin et al., 2013; Net et al., 2014b, 2015a, 2015b).

Because of their toxic, carcinogenic and mutagenic effects (IARC, 2010; Straif et al., 2005) sixteen PAHs have been listed as priority substances by the United State-Environmental Protection Agency (US-EPA, 2013; US-Department of Health and Human Services (1995)). PCBs exposure may cause endocrine disruption, abnormalities of skin and liver function, trouble in immune systems, dysfunction of neurological development and the reproductive system (Longnecker et al., 1997). PCBs have been now listed as POPs in the Stockholm convention.

For the aquatic environment, studies have focused mainly on organic contaminants occurrence in dissolved and/or sedimentary phases. To our lnowledge, there is a lack of data on the distribution of these compounds in the particulate phase of the water column. In the present work, the aims were firstly to evaluate the distribution of PCBs, PAHs and Me-PAHs in the dissolved, particulate and sedimentary phases of freshwater systems. Fifteen sampling sites located in six rivers at the cross-border area of Northern France-Belgium were studied. Secondly, the origins of contamination and the potential environmental risks were investigated.

2. Materials and methods

2.1. Chemicals and materials

Mixed standard solutions of PAHs and Me-PAHs were purchased from Restek Corp (Bellefonte, PA, USA) and PCBs standard solutions were from Accustandard, Inc. (New Haven, CT, USA). Acenaphthene-d10 (A-d10), naphtalene-d8 (N-d10), perylene-d12 (Per-d12), phenanthrene-d10 (Phe-d10) and pyrene-d10 (Pyr-d10) were were obtained from LGC-Promochem (Middlesex, UK) and used as internal standards for PAHs and Me-PAHs quantifications. Tetrachloronaphtalene (TCN), 2,3,3',5,6-tetrachlorobiphenyl (PCB112) and octachloronaphtalene (OCN), used for PCBs quantification were purchased from Dr Ehrenstorfer (Augsburg, Germany). HPLC-grade solvents (hexane, dichloromethane (DCM), acetone, propan-2-ol and methanol) were purchased from Dislab (France). Ultrapure Water (Milli Q), with 18.2 MΩ/cm resistivity (Milli-Q) was produced from a Millipore apparatus. C_{18} SPE cartridges (200mg/6mL) were purchased from Sigma-Aldrich (Saint-Louis, USA). Merck silica gel 60 (70-230 mesh) activated at 450°C was heated at 120°C for 12 h prior to use. Glassware was systematically washed with detergent (Decon, East Sussex, UK) and acidified ultra-pure water, rinsed with ultrapure water followed by acetone then dried at 120°C prior to use.

2.2. Sampling sites

The studied area is part of the watershed of the Scheldt (Fig. 1), which is surrounded by areas of high anthropogenic activity and high population density. Historically, industrialization has been among the highest in Europe (Lesven et al., 2009; Net et al., 2014a, 2015b). Although mining and metallurgical activities in the Scheldt basins have been reduced in recent decades, the remobilization of metal trace elements buried in sediments since the beginning of the industrial era is one of the major sources of pollution today (Lesven et al., 2009). However, only few data on organic contaminants are available in the literature (Net et al., 2014a, 2015b). The sampling was conducted in early spring 2014 in fifteen sites located at the cross-border areas of rivers and streams located at the cross-border areas of northern France-western Belgium and the watershed upstream of the Scheldt (Fig. 1). The Scheldt is a 350 km long river and crosses northern France, western Belgium and southwestern Netherlands. It is mainly channeled and crosses five regions where it receives various wastewaters and effluents before discharging into the North Sea near Vlissingen. The present study focuses on the watercourses and rivers located at the cross-border region of northern France-Belgium. Six sites were located along the Scheldt (Fresnes, Neuville, Crevecoeur, Warcoing, Berchem, Zingem), three on the Lys River (Aire sur-la-Lys, Erquinghem-Lys, Wervicq), two in the Deûle River (Don and Wambrechies), two in the Scarpe River (Brebière and Nivelle), one in the Sensée River (Férin) and one in the Sambre River (Jeumont) (Fig. 1; Table 1).

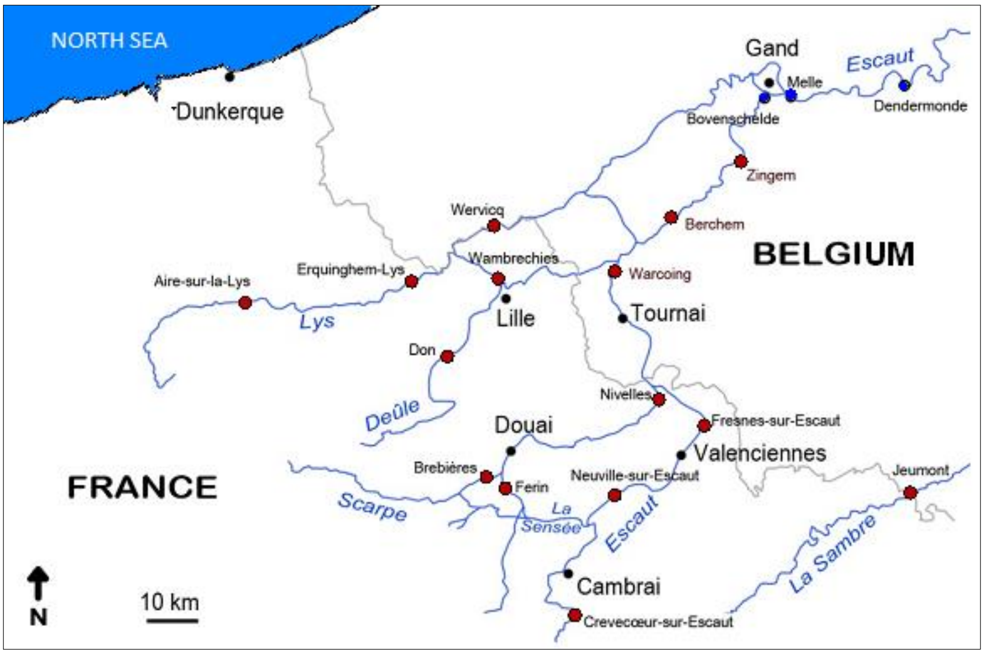

Fig. 1. Studied sites at the cross-border area Northern France-Belgium (red points).

Table 1: Location of the sampling sites and their physicochemical characteristics of the water body.

Rivers	***Sampling sites***	***GPS coordinates***	***pH***	***T (°C)***	***O_2 (mg/L)***	***Turbidity (F.N.U)***	***E (mV)***	***SSM (mg/L)***	***COD (mg/L)***	***SO_4^{2-} (mg/L)***	***Cl^- (mg/L)***	***NO_3^- (mg/L)***
The Scheldt	Zingem	N50°53'36,30" E3°40'50,07"	-	14.3	10.9	19.5	146	26.8	3.6	102.0	68.8	32.8
	Berchem	N50°47'36,71" E3°30'16,74"	-	15.2	10.6	34.6	260	88.9	5.4	99.5	74.4	30.3
	Warcoing	N50°42'2,18" E3°21'8,90"	-	15.0	10.6	28.9	288	44.7	3.5	103.8	59.8	36.9
	Crevecoeur	N50°06'16,2" E3°14'51,1"	6.80	12.2	11.6	8.0	315	11.6	4.0	19.2	30.6	37.1
	Neuville	N50°18'05,9" E3°21'01,1"	7.24	14.1	12.4	17.7	305	16.7	2.0	31.4	47.7	28.8
	Fresnes	N50°25'33,0" E3°34'52,7"	7.51	13.7	11.0	14.2	283	20.1	2.2	50.7	50.6	28.9
The Lys	Wervicq	N50°46'36" E3°02'35"	-	14.8	6.5	25.4	134	47.3	3.5	84.0	74.2	32.8
	Aire sur la Lys	N50°38'45,1" E2°24'34,8"	7.20	14.4	8.9	38	252	17.8	2.6	104.2	65.1	47.9
	Erquinghem-Lys	N50°40'37,8" E2°50'08"	6.92	13.7	7.2	11.7	301	12.2	3.4	53.4	62.6	24.9
The sensée	Férin	N50°32'23,8" E3°07'24,9"	7.56	14.7	8.6	5.9	258	6.0	1.9	30.4	42.1	27.3
The Sambre	Jeumont	N50°17'52,6" E4°06'.05,4"	7.98	13.7	10.8	11.6	262	17.6	4.4	36.6	31.9	13.8
The Deûle	Wambrechies	N50°41'10" E3°03'10"	6.85	14.6	6.2	25.4	243	24.0	3.2	99.8	77.7	32.0
	Don	N50°32'48,8" E2°55'14,7"	6.91	14.3	9.3	9.1	133	9.6	2.2	83.4	57.3	37.0
The Scarpe	Brébières	N50°33'47" E3°03'23,3"	7.57	12.6	11.0	4.5	292	5.6	2.0	31.4	37.7	38.5
	Nivelles	N50°28'11,6" E3°27'58,1"	7.65	14.4	10.3	26.2	335	34.8	6.2	175.7	68.5	17.4

2.3. Sampling

Water was collected using 2.5 L pre-cleaned amber glass bottles that were immediately capped with Teflon-lined lid. Sediment samples were collected from the top layer 0 - 5 cm using 10 cm diameter and 30 cm long polycarbonate tubes. The sediments were kept in pre-calcinated aluminum containers that capped with aluminum foil. The samples (water and sediment) were transported to the laboratory and directly treated without storage.

2.4. Targeted analytes

In this work, the following PCBs, PAHs and Me-PAHs were analyzed:
16 PAHs: naphthalene (N), acenaphthylene (Ayl), acenaphthene (Aen), fluorene (F), anthracene (Ant), fluoranthene (Fl), benz[a]anthracene (BaA), chrysene (Ch), benz[a]pyrene (BaP), phenanthrene (Phe), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[ghi]perylene (Bghi), dibenzo[a,h]anthracene (DhA), indeno[1,2,3-cd]pyrene (IP), pyrene (Pyr).

18 Me-PAHs: 1-methylnaphthalene (1M-N), 2-methylnaphthalene (2M-N), 1,2-dimethylnaphthalene (1,2DM-N), 1,6-dimethylnaphthalene (1,6DM-N), 2,6-dimethylnaphthalene (2,6DM-N), 1-methylphenanthrene (1M-Phe), 2-methylphenanthrene (2M-Phe), 3-methylphenanthrene (3M-Phe), 9-methylphenanthrene (9M-Phe), 2-methylanthracene (2M-An), 1,7-dimethylphenanthrene (1,7-DMP), retene, 1-methylfluoranthene (1M-Fl), 3-methylfluoranthene (3M-Fl), 1-methylpyrene (1M-Pyr), 4-methylpyrene (4M-Pyr), 3-methylchrysene (3M-Ch), 6-methylchrysene (6M-Ch).

(28 PCBs: 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206, 209.

The physicochemical properties of each compounds are presented in Table 1S in supporting Information (SI). The behavior and fate of organic contaminants in the environment are controlled by their physicochemical properties such as water solubility (S_W), Octanol-Water partition coefficient (K_{OW}) and organic carbon partition coefficient (K_{OC}) which are generally presented by log K_{OW} and log K_{OC}. S_W controls the distribution between water, SSM and sediment. K_{OW} predicts the tendency of a contaminant to concentrate in aquatic organisms, while logK_{OC} indicates the capacity to bind to organic matter in SSM or sediment. S_W values of PAHs and Me-PAHs are low and decreases with the increase in the number of aromatic ring (Table 1S). Log K_{OW} and log K_{OC} of PAHs and Me-PAHs increase with the increase in the number of cycles, which suggest that high molecular weight PAHs in aquatic environment will be appreciably sorbed to SSM, aquatic organism and sediment. Similarly, PCBs have low S_W and high values of log K_{OW} and log K_{OC} (Table 1S).

2.5. Sample extraction

On arrival at the laboratory, water samples were directly filtered using calcinated 0.45 µm Whatman glass microfiber filters(GF/F). Targeted compounds in dissolved phases were extracted using solid phase extraction (SPE), while compounds associated to SSM and sediments were extracted using accelerated solvent extraction or ASE (ASE200, Dionex Corp., USA).

2.5.1. SPE extraction

Filtered water samples were spiked with internal standards prior to extraction. An SPE procedure using C-18 cartridges was performed according to the method developed by Busetti et al. (2006). Briefly, cartridges were conditioned with 9 mL of acetonitrile, 9 mL of 2-propanol and 12 mL of a mixture of MilliQ water/2-propanol (85:15, v/v) acidified to pH 2.5. The samples were then passed through the cartridges (1 drop/second). Cartridges were washed with 30 mL of Milli-Q water/2-propanol mixture (85:15, v/v) acidified at pH 2.5 and then dried under nitrogen-flow for 10 mn. Targeted compounds were eluted with 12 mL of hexane/2-propanol/acetone mixture (90:5:5, v/v/v) followed by 3 mL of DCM. The extracts were then concentrated to 50-200 µL under nitrogen-flow and stored at 4°C until GC-MS analysis.

2.5.2. ASE extraction

For the targeted compunds associated with SSM the extractions were performed on dried SSM obtained from 2.5 L of water sample. Sediment were dried, finely ground and sieved at 224 µm prior extraction. Each sample was spiked with internal standards and first extracted with DCM/acetone (v:v 1/1) according to the method developed by Reid et al. (2009). A second extraction was performed with DCM according to the method developed by Tronczynski et al., (2005). The extracts of each sample were combined before the purification step.

2.6. Purification and separation

Molecular sulfur was removed by addition of activated metallic copper to the extracts. The extracts were concentrated, solvent-exchanged to hexane and purified on a silica column. In the top of column, 2 g of anhydrous sodium sulfate was added to eliminate eventual traces of water. Targeted compounds were recovered by successive elution with 20 mL of hexane, 15 mL of hexane/DCM mixtures (3:1, v/v) followed by 15 mL of hexane/DCM mixture (1:1, v/v) and 15 mL DCM. Each sample was concentrated to 200 µL for SSM and 100-500 µL for sediments.

2.7. GC-MS analysis

Each compound was analyzed using a Varian 3900 gas chromatograph (GC) equipped with a deactivated fused-silica guard column (5 m, 0.25 mm i.d.) and a fused-silica capillary Phenomenex XLB (60 m length, 0.25 mm i.d., 0.25 µm film thickness) and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS). The carrier gas was helium, held at a constant flow rate of 1 mL/min. Samples were injected in the splitless mode at 280°C and the injector was purged with helium after 1 min. Each group of organic compounds was analyzed separately. The transfer line and the ion trap were held at 280°C and 220°C respectively. The oven temperature was programmed as follows: from 70°C (1 min) to 170°C at 10°C/min, then ramped at 4°C/min to 230°C, and then at 3°C/min (13 min) to 300°C for HAPs and Me-HAPs. For PCBs, the oven temperature was programmed from 80°C (1 min) to 170°C at 10°C/min, then to 230°C at 4°C/min, and finally to 300°C at 3°C/min (19 min).

Each targeted compound was identified based on the retention time and the mass spectrum from a chromatogram of standard solutions acquired in full scan mode. Quantification was then performed in the MS/MS or multiple residual monitoring (MRM) modes for better selectivity.

2.8. Quantative analysis and quality control

For the quantification, a six-point internal calibration method was used. Internal standards were added for each calibration point in order to better fit to the properties of targeted compounds. To minimize the error of quantification, the procedural blank for the entire analytical procedure was performed in triplicate together with each environmental sample batch. Our results showed that the procedural blanks were free from any targeted PCBs, PAHs and Me-PAhs. This ensures that no significant contamination occurs during the procedure.

Limits of quantifications (LOQs) were estimated in the range of 0.3-5, 18-38 and 0.5 µg/kg dw of sediment respectively for PAhs, Me-PAHs and PCBs. For water, LOQs were determined at 3-50, 1.5-3 and 5 ng/L respectively for PAhs, Me-PAhs and PCBs. Recoveries of PCBs, PAHs and Me-PAHs were calculated by spiking the targeted compounds into environmental matrices of interest (filtered river water, SSM retained on GF/F and sediment). The recovery rates obtained for solid matrices were >79% for PAHs, >73% for Me-PAHs and >75% for PCBs. For the dissolved phase, the recoveries of PAHs and PCBs were estimated at > 76% and >68% respectively.

3. Results and discussion

3.1. Physicochemical characteristics of water samples

During the sampling, classical parameters such as pH, temperature (T), dissolved oxygen (O_2), turbidity, and potential (E) have been measured directly on field for better understanding the characteristic of water body. In the laboratory, sulfate (SO_4^{2-}), chlorine (Cl^-) and nitrate (NO_3^-) ions were also measured using ionic chromatography. The SSM content was determined by weighing. Dissolved organic carbon (DOC) which refers to the dissolved fraction of organic carbon that passes through 0.45 µm GF/F was also determined. The values of these parameters are listed in Table 1. Generally, the water bodies were relatively neutral with pH values of 6.80-7.98 and well oxygenated with dissolved oxygen ranged between 6.2 and 11.6 mg/L. The temperature was ranging from 12.2 to 15.2°C. However, SSM content was highly variable ranging from 5.6 at Brebières to 88.9 mg/L at Berchem. Nitrate concentrations were detected at high levels up to more than 25 mg/L except for Nivelles and Jeumont (Table 1). Based on the values of nitrate, these surface waters were classed as quality 2. For other parameters, the measured values were quite variable and of doubtful use to judge the quality of the water bodies may indicate that these rivers could be significantly influenced by agricultural activities. Indeed, the principal origin of nitrates is the leaching of agricultural soils (Billen et al., 2005).

3.2. Occurreence in the three phases

The occurrence of Σ_{28}PCBs, Σ_{16}PAHs and Σ_{18}Me-PAHs both in water column (dissolved and particulate phases) and in sediment was investigated. The total concentrations of each group of compounds varied significantly between stations and phases (Table 2S). High levels of Σ_{16}PAHs in SSM were identified at Zingem (3.74±0.15 µg/L), Berchem (3.58±0.2 µg/L), Warcoing (3.10±0.15 µg/L) and the highest was detected at Wervicq (4.94±0.25 µg/L). The great majority of Σ_{16}PAHs associated with the SSM with an average of 80% versus only 20% in dissolved phase (Table 2S). This can be explained by the fact that PAHs have high affinity for solid matrices due to their low S_W and high K_{OW} and K_{OC} (Table 1S). In sediment, the Σ_{16}PAHs were detected at high levels ranging from 3.75±0.19 to 22.30±1.11 mg/kg dw with an average value of 9.01±6.69 mg/kg dw (Fig. 2a, Table 2S). Above all the highest amount of dissolved-PAHs were detected in the Lys River. However, particulate-PAHs were detected at high levels in the Scheldt, Lys and Deûle Rivers (Fig. 2b). For sediment, the Deûle River was the most contaminated by PAHs (Fig.2b). In contrast, the Σ_{18}Me-PAH associated with SSM was a minority (19%) compared to dissolved phase (81%) (Fig. 3a). in the water column, the highest concentration for global contamination was found at Aire-sur-la-Lys (4.40± 0.22 µg/L) for the sum of dissolved phase and particulate phases (Σ_{D+P}) followed by Brebières (4.19±0.21 µg/L for Σ_{D+P}). In sediment, the Σ_{18}Me-PAHs were detected at high levels ranging from 0.17±0.01 to 2.62±0.13 with an average of 1.11±0.99 mg/kg dw. However, Σ_{18}Me-PAHs was nine times lower compared to Σ_{16}PAHs. A high degree of heterogeneity in each river was also observed (Fig.3b). Highly variable concentrations of both PAhs and Me-PAHs were observed between stations for each river (Fig. 2-3). This may be due to their local sources located near to the sampling site. Above all the Lys River seems to be the most contaminated by PAHs and Me-PAHs in the dissolved phase.

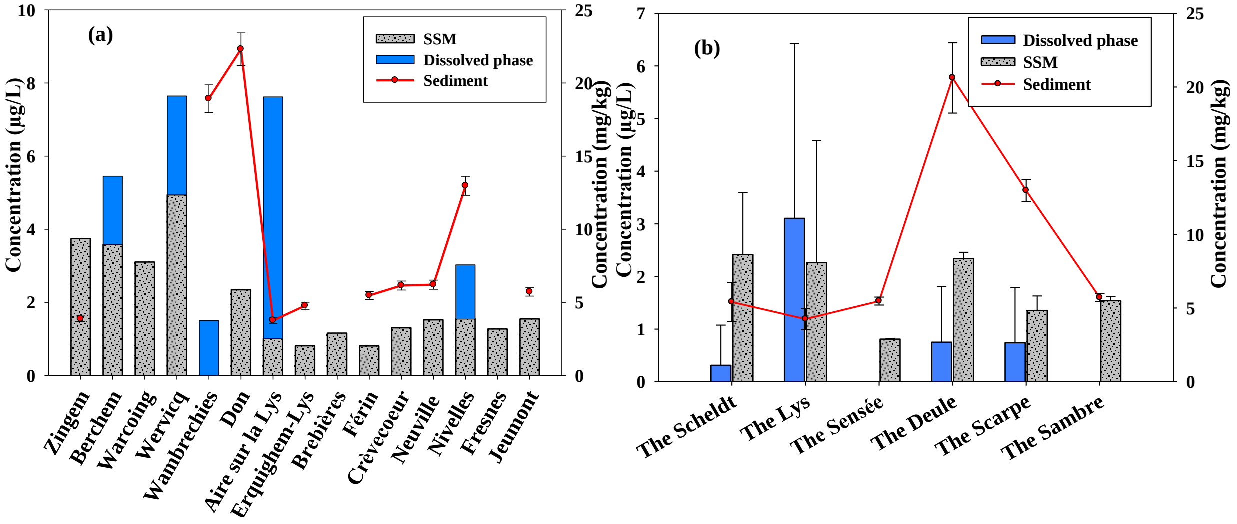

Fig. 2. Comparison of Σ_{16}PAHs contents in dissolved phase, associated with SSM and in sediment for each (a) station and (b) river.

For PCBs, only PCB153 was detected among the 28 PCBs congeners. Similar observation was found in previous study for the Scheldt Estuary with dominance of PCB153 (Van Ael et al., 2012). However, our results showed that PCB153 was not detected in dissolved phase (Table 2S, Fig. 4a, b). In SSM, PCB153 was not detected for the majority of stations, the exceptions being Wervicq, Aire sur la Lys and Nivelles (Fig. 4a, Table 2S). Although, PCB153 was detected in SSM for three sampling sites, the contamination levels were relatively low. In sediments, PCB153 was detected at all sampling sites but the concentrations were relatively low in the range of 0.23 - 7.34 µg/kg dw (Fig. 4a, Table 2S). Indeed, PCB153 has a strong affinity to accumulate into biota, SSM and sediment due to its high K_{OW} and K_{OC}. Previous studies showed that PCBs still present in water body and sediment in freshwater in Northern France and in Belgium (Net et al., 2015a; Van Ael et al., 2012, 2013). Their presence in the aquatic environment may be due to their high persistence and their atmospheric deposition from the permanent combustion process emissions (incinerator) or their release from old electronic equipment. Above all, PCB153 was detected at low levels in each river; <LOQ in dissolved phase, <13 ng/L associated with SSM and <8 µg/kg dw in sediment (Fig. 4b).

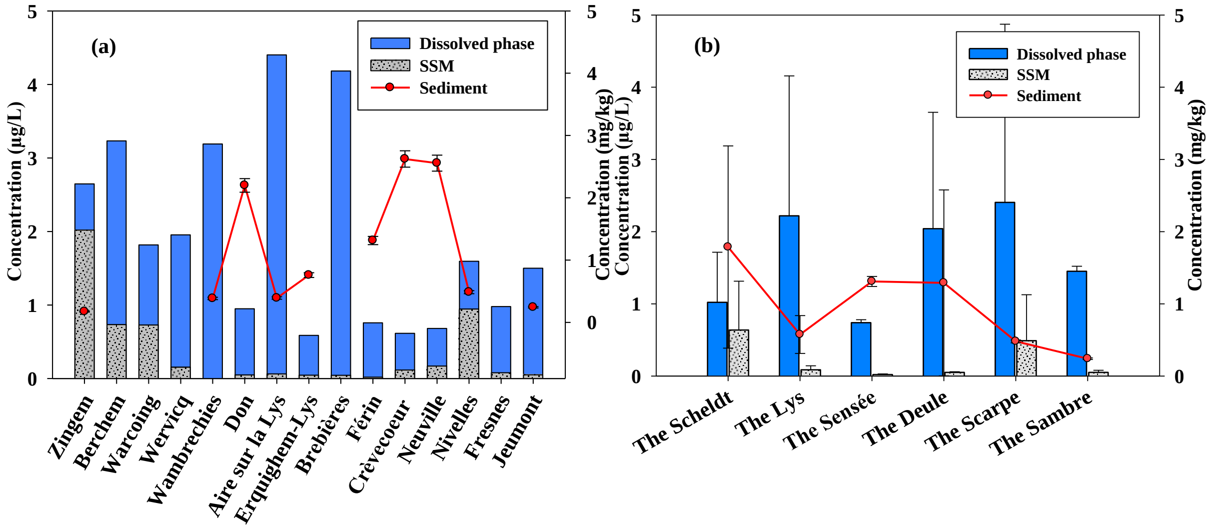

Fig. 3. Comparison of Σ18Me-PAHs contents in dissolved phase, associated with SSM and in sediment for each (a) station and (b) river.

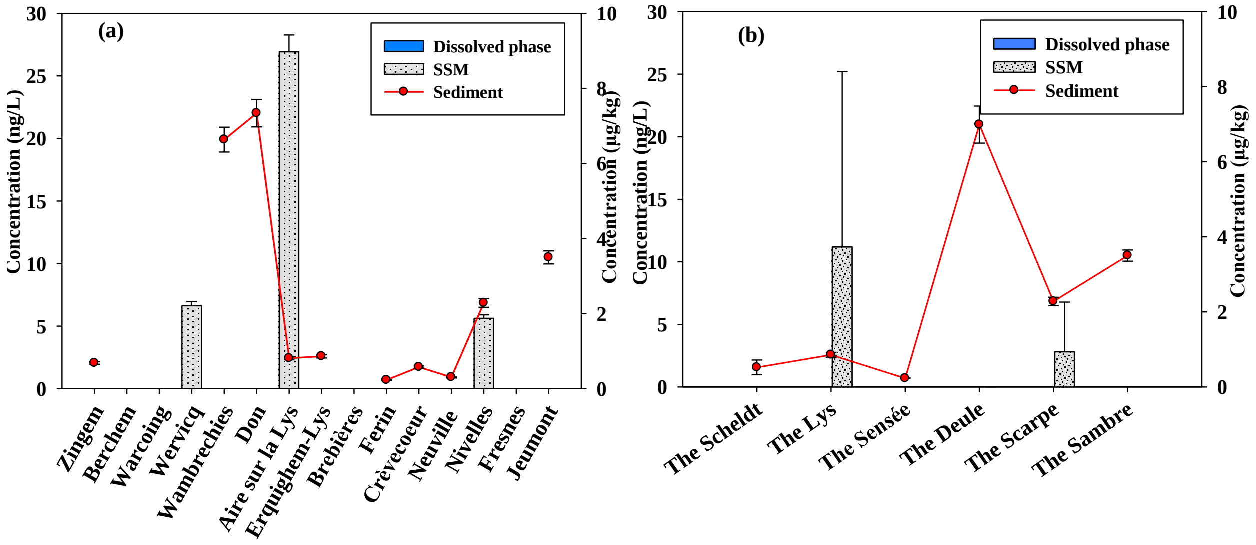

Fig. 4. Distribution of PCB153 in dissolved phase, associated with SSM and in sediment for each (a) station and (b) river.

3.3. Distribution of individual compounds in the three phases

For PAHs, the global contamination of the water columns was dominated by the low molecular weight PAHs (LMW; 2-3 aromatic rings). For all stations, LMW-PAHs exceeded 50% of the total contamination (Σ_{D+P}) (Fig. 5a). The highest level of contamination was recorded at Aire* sur-la-Lys where naphtalene was abundant (4.29±0.20 µg/L). In contrast, high molecular weight PAHs (HMW; 4-6 aromatic rings) were predominant in sediments (Fig. 5c). 87% of 4-6 aromatic rings PAHs were detected in sediments versus only 13% of 2-3 aromatic rings PAHs. This distribution was similar to that previously reported for rivers located in highly industrialized zones (Kanzari et al., 2014). Our results can be explained by the fact that HMW-PAHs are hydrophobic and more easily sorbed in a solid matrix due to their low S_w, high K_{oc} and K_{ow} (Table 1S) (Chen et al., 2004; Patrolecco et al., 2010). Fig. 6a-b shows the distributions of individual PAHs versus Log K_{ow} and S_w. The proportion of PAHs in the particulate phase increases with increasing log K_{ow}. PAHs with log $K_{ow} \geq 4.45$ were detected mainly in the particulate phase (Fig. 6a). Similarly, the distribution of PAHs depends on S_w. PAHs with $S_w <$ 1 mg/L were not detected in the dissolved phase (Fig. 6b) because they accumulate preferentially into SSM and sediments. Me-PAHs, 2-3 aromatic rings represent ~ 100% of Σ_{D+P} for all stations (Fig.5b). However, 4 aromatic rings Me-PAHs were predominant in sediment (Fig. 5d). In water column, Me-PAHs present mainly in dissolved phase and 9-methylphenanthrene and 2-methylanthracene were predominant. Fig. 7a-b shows the correlation between the distribution of individual Me-PAHs and their physicochemical properties. The percentage of Me-PAHs in dissolved phase decreases with decreasing S_w (Fig. 7b). For PCBs, as reported previously, only PCB153 in the dissolved phase can be explained by the fact that this compound has very low solubility (0.001 mg/L) and high K_{oc} and K_{ow}.

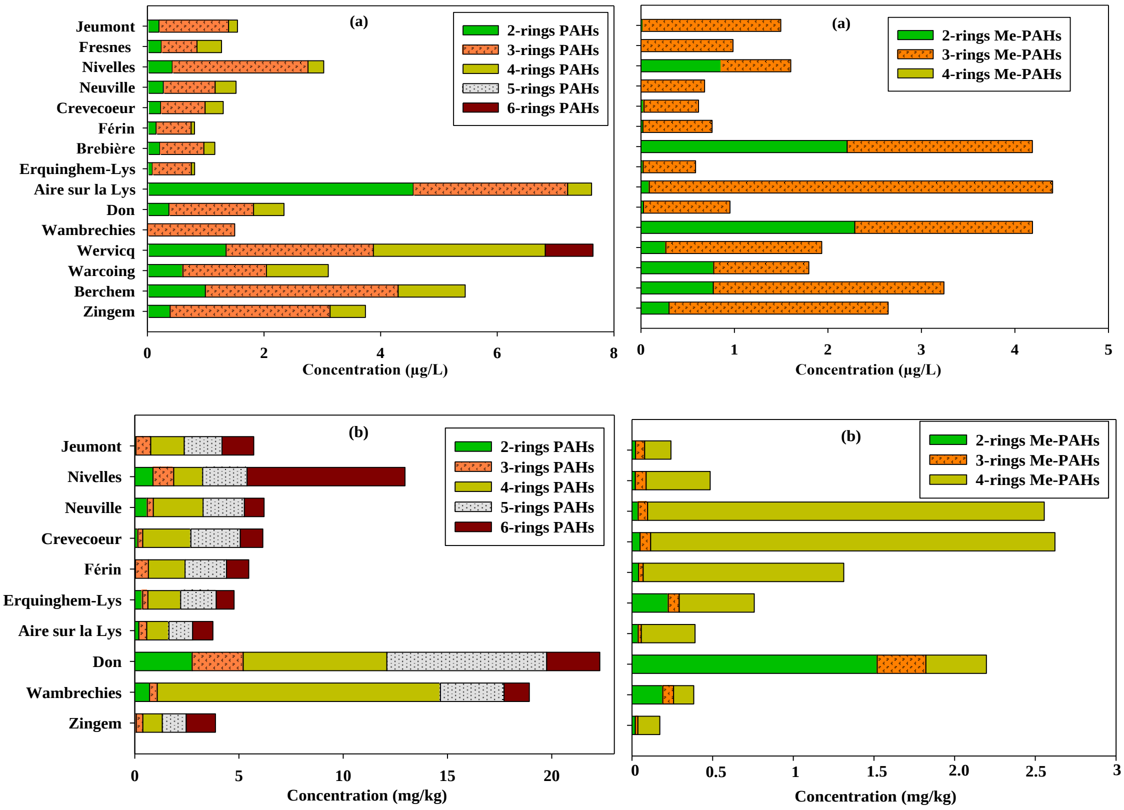

Fig. 5. Distribution of Distribution of PAH and Me-PAH: (a) and (b) in water for the sum of dissolved and particulate phases (ΣPAH_{D+P}) and (c) and (d) in sediment.

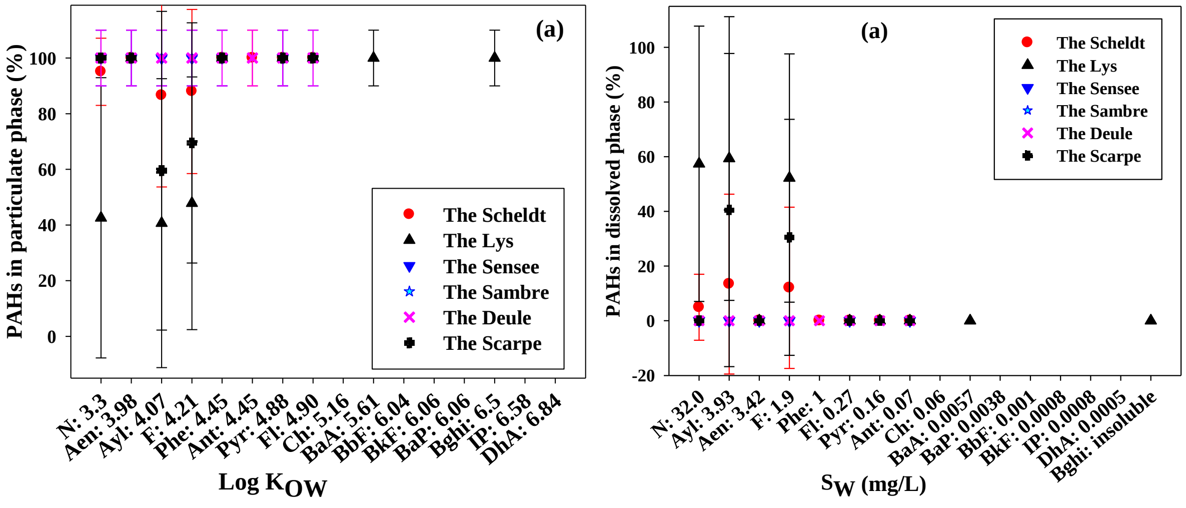

Fig. 6. Percentage of individual PAH (a) in particulate phase ([PAH] in SSM/([PAH] in SSM + [PAHs] in dissolved phase)*100) versus Log KOW and (b) in dissolved phase ([PAH]in dissolved phase/([PAH]in SSM +[PAHs]in dissolved phase)*100) versus water solubility (SW) for the average of each river.

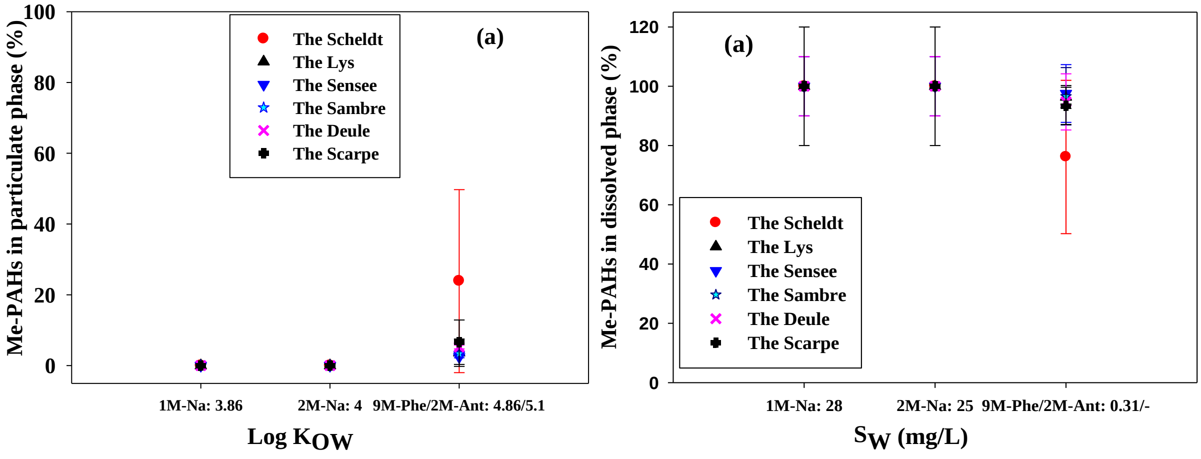

Fig. 7. Percentage of individual Me-PAH (a) in particulate phase ([Me-PAH] in SSM/([Me-PAH] in SSM + [Me-PAHs] in dissolved phase)*100) versus Log KOW and (b) in dissolved phase ([Me-PAH]in dissolved phase/([Me-PAH]in SSM +[Me-PAHs]in dissolved phase)*100) versus SW for the average of each river.

3.4. Source apportionment

PAHs can originate from natural and anthropogenic processes (Yunker et al., 2002), while PCBs are chemically synthesized and have no natural source (Wolska et al., 2012). Atmospheric transport/deposition, industrial and municipal effluents, domestic sewage and urban runoff can be the major point-source or non-point source of PAHs and PCBs in aquatic environments (Bakarat et al., 2013; Manoli and Samara, 1999; Net et al., 2015a; Zhu et al., 2004).

The sources of parent and alkylated-PAHs can be investigated by diagnostic of different PAH isomer ratios (Miki et al., 2014; Net et al., 2014a; Scolo et al., 2000). Isomer ratios BaA/(BaA+Ch) and IP/(IP+Bghi) represent a reliable tool due to their stability (Yunker et al., 2002). BaA/(BaA+Ch) ratio <0.2 usually implies a petroleum source, 0.2-0.35 indicates a mixed source (petroleum/combustion) and >0.35 indicates a combustion origin. Similarly, IP/(IP+Bghi) ratio <0.2 indicates a petroleum origin, 0.2-0.5 indicates a mixed source and >0.5 indicates a biomass/coal combustion source. In addition, the ratio MPhe/Phe defined as the ratio of the sum of all detected methylated phenanthrenes (3M-Phe+2M-Phe+9M-Phe+1M-Phe) to Phenanthrene was also used to complement the source identification (Barakat et al., 2011). LMW-PAHs were the contaminants at five stations (Fig. 5a) suggesting both petrogenic and combustion sources for PAHs in the water column (Zhang et al., 2004). Moreover, naphthalene, acenaphthylene and fluorene are among the predominant LMW-PAHs in the gas phase of the atmosphere, therefore hydrocarbons detected in the studied sites might originate from atmospheric fallout/deposits (Ruiz-Fernández et al., 2014). The cross plots of IP/(IP+Bghi) and MPhe/Phe versus BaA/(BaA+Ch) in sediment (Fig.8a-b) indicated that PAhs originated mainly from combustion sources; except for Férin and Neuville sites where mixed sources were identified. Such a strong pyrogenic signature of PAHs was confirmed by the abundance of HMW-PAHs (Fernández et al., 2000). This fact has been reported as evident in most urban sediments (Stout et al., 2004), industrial countries and zones historically containing coal/oil tar production, processing and operations. In our case, auto/diesel/gas engine emissions represented the minor source of PAHs except in Nivelles station where the vehicle emissions tracer IP exceeded 50% of Σ_{16}PAHs. Other compounds such as Bghi and BkF can be also used as auto tracers (Li et al., 2012). In our case, these compounds were detected as <10% of Σ_{16}PAHs. Crude oil, wood and Coal combustion might be the exclusive combustion origin since the markers Pyr, Fl, Phe and Ant were observed in the majority of samples (Larsen and Banker; 2003; Zhang et al., 2012).

The origin of PCBs has been usually identified by evaluating the similarity of the PCB patterns found in the samples compared to the principal commercial PCB mixtures (Aroclor) (Net et al., 2015a) or by examining the correlation between PCBs and other parameters (e.g. PAHs)

(Merhaby et al., 2015; Wolska et al., 2014). Our results showed a linear correlation between PCB153 and Σ_{16}PAHs concentrations (R^2= 0.83, p<0.01), suggesting their similar sources of emission. Therefore, PCB153 are most likely originated also by the pyrolysis processes such as coal, wood and peat combustion (Rose et al., 2004; Ruiz-Fernández et al., 2012).

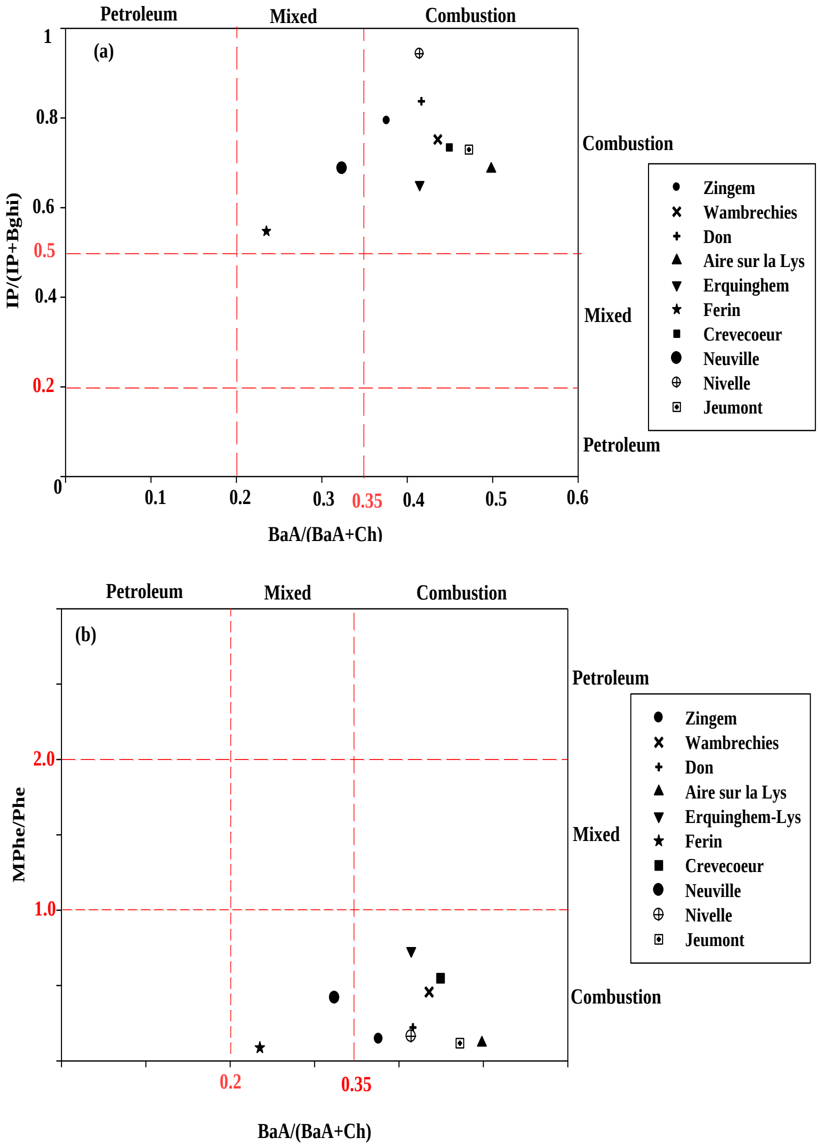

Fig. 8. Cross plots of (a) IP/(IP+Bghi) and (b) MPhe/Phe versus BaA/(BaA+Ch) for sediment samples.

3.5. Ecotoxicological state

Sediment Quality Guidelines (SQGs) have been established using different procedures for assessing the sediment quality and the ecotoxicological risk. Since similarities have been found between existing SQGs in many cases, “concensus” guidelines were developed to unify guidelines and to take into account the mixture effects (Macdonald et al., 2000; Swartz, 1999). Our results were compared to the numerical consensus-based SQGs (CBSQGs) which include the Threshold Effect Concentration (TEC; concentration below which adverse effects on sediment-dwelling organisms are not expected to occur), the Probable Effects Concentration (PEC; concentration above which adverse effects on sediment-dwelling organisms are likely to be observed) and the Midpoint Effect Concentration (MEC=TEC+PEC/2). MEC was recommended to better interpret the potential impact of contaminants concentrations between the TEC and PEC values that is not included in the CBSQGs (Doyle et al., 2003). The ecotoxicological risk of the studied sites is illustrated for four levels of sediment quality: 1(≤CBTEC), 2 (>CBTEC and ≤MEC), 3 (>MEC and ≤CBPEC) and 4 (>CBPEC) (Table 2, Fig. 9). Based on PCBs, quality 1 was assigned to all of the rivers. PCB153 was <CBTEC which predicts the absence of toxicity to benthic dwelling organisms based on this parameter. However, based on Σ_{16}PAHs, 70% of stations were identified as quality 2 and 30% identified as quality 3. Don, Wambrechies and Nivelles present the highest ecotoxicological risk. Based on individual compounds, dibenz(a,h)anthracene was noted as the main pollutant, detected at 80% of the stations. Its concentration exceeded generally recommended CBPEC which implies that biological adverse effects are expected to occur. On the other hand, naphthalene, phenanthrene, anthracene and fluorene were frequently detected (60-80%) but their individual amounts were <CBTEC. 2-methylnaphthalene was detected in the majority of stations (90%) and was detected frequently >CBPEC which implies possible adverse effects on sediment-dwelling organisms. Based on 2-methylnaphthalene, the majority of the stations was identified as quality 4.

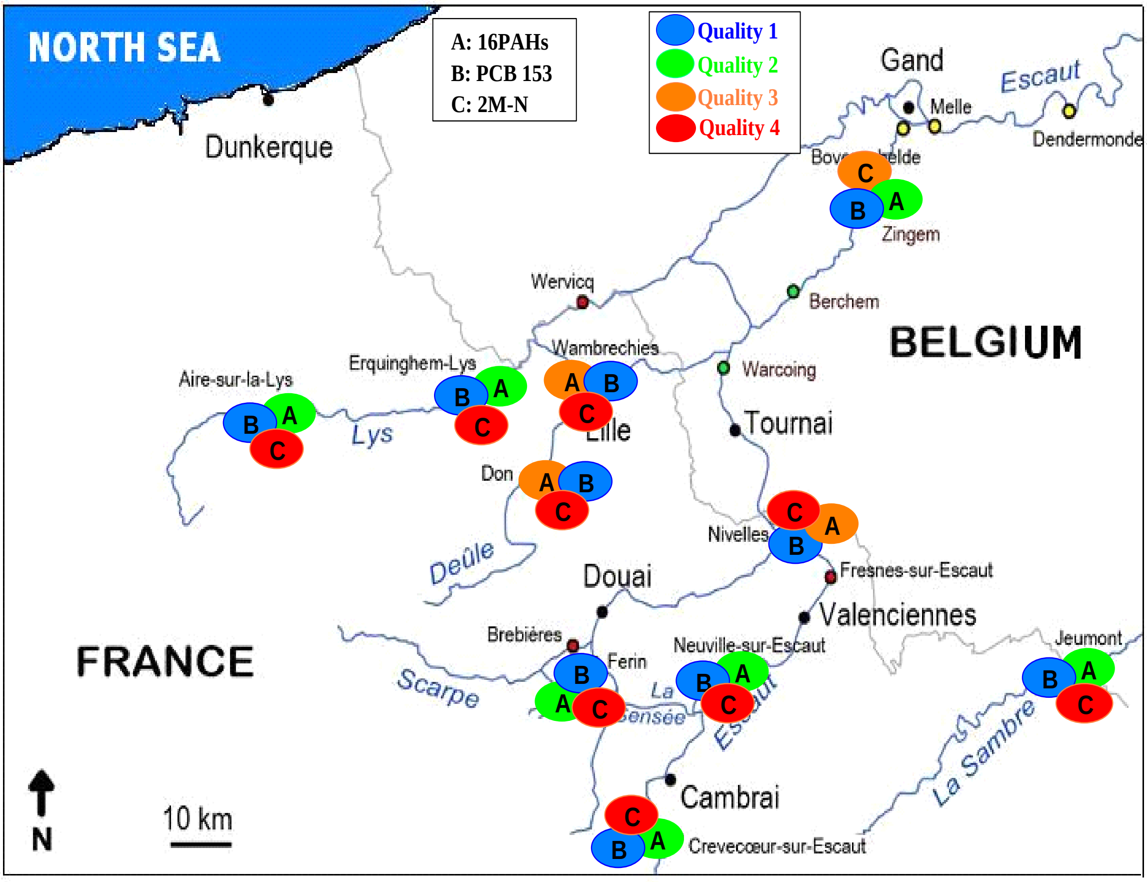

Fig. 9. Ecotoxicological risk of each site based on Σ_{16}PAHs and PCB153 and 2-methylnaphthalene.

Table 2: Consensus-based SQGs based on individual and total PAHs, 2-methylnaphthalene, total PCBs and quality of studied stations.

				Concentrations (µg/kg dw)													
				The Scheldt			**The Deûle**		**The Lys**		**The Sensée**	**The Scarpe**	**The Sambre**				
	µg/kg dw													**% Station**			
Compounds	**CBSQGs TEC**	**MEC (TEC+PEC) /2**	**CBSQGs PEC**	**Zingem**	**Crèvecœur**	**Neuville**	**Wambrechies**	**Don**	**Aire sur la Lys**	**Erquinghem**	**Ferin**	**Nivelles**	**Jeumont**	**Quality 1**	**Quality 2**	**Quality 3**	**Quality 4**
Naphthalene	176	369	561	75.7	150.5	604.1	715.9	2755.2	197.8	381.3	33.8	875.5	60.8	40	10	10	40
Acenaphthylene	5.9	67	128	71.2	34.9	33.9	41.8	187.4	73.4	45.9	113.6	183.6	51.1	0	50	30	20
Acenaphthene	6.7	48	89	36.8	32.6	73.9	102.6	676.4	37.9	45.5	65.8	119.6	18.4	0	50	20	30
Fluorene	77.4	307	536	60.6	16.8	18.5	20.9	79.7	63.6	25.0	67.2	201.7	57.5	80	20	0	0
Phenanthrene	204	687	1,170	114.4	121.8	140.6	148.2	1369.9	162.0	93.6	335.7	416.0	491.4	60	30	0	10
Anthracene	57.2	451	845	32.6	28.7	24.3	54.6	136.7	41.0	44.2	40.9	73.7	90.9	70	30	0	0
Fluoranthene	423	1327	2,230	190.5	546.5	582.4	665.8	2393.6	223.1	362.9	404.8	309.1	407.1	60	30	0	10
Pyrene	195	858	1,520	421.0	1149.6	1246.1	12436.5	3468.9	387.3	788.6	897.0	722.2	748.3	0	50	40	10
Benz(a)Anthracene	108	579	1,050	120.6	275.8	180.2	208.6	427.4	228.3	173.7	107.1	149.7	214.3	10	90	0	0
Chrysene	166	728	1,290	200.4	338.1	376.7	270.1	598.6	230.0	245.5	348.4	211.5	239.5	0	100	0	0
Benzo(b)fluoranthene	240	6,820	13,400	579.2	1411.1	1148.2	1941.4	4983.6	586.9	948.9	1099.3	1276.1	1044.6	0	100	0	0
Benzo(k)fluoranthene	240	6,820	13,400	229.7	354.6	340.1	413.3	963.2	215.7	268.7	329.5	342.7	307.6	20	80	0	0
Benzo(a)pyrene	150	800	1,450	224.5	292.4	253.8	277.3	546.7	233.5	279.8	240.8	241.0	228.0	0	100	0	0
Indeno(1,2,3-cd)pyrene	200	1,700	3,200	1112.4	796.1	650.2	912.2	2129.7	668.6	555.3	582.1	7149.5	1110.3	0	80	10	10
Dibenz(a,h)anthracene	33	84	135	115.6	309.9	236.7	416.9	1173.8	98.7	207.0	324.9	236.9	227.5	0	0	20	80
Benzo(g,h,i)perylene	170	1,685	3,200	228.5	288.2	295.5	300.8	413.9	305.5	297.4	481.3	429.8	411.6	0	100	0	0
ΣPAH	1,610	12,205	22,800	3873.6	6147.4	6205.1	18926.6	22304.5	3753.2	4763.3	5472.2	12965.2	5708.9	0	70	30	0
2-methylnaphthalene	20.2	111	201	174.9	2623.8	2556.5	384.7	2199.1	392.0	759.9	1314.0	486.8	243.3	0	0	10	90
ΣPCBs	60	368	676	0.7	0.6	0.3	6.6	7.3	0.8	0.9	0.2	2.3	3.5	100	0	0	0

[a]CCME, 1999

Conclusion

The occurrence of PAHs, Me-PAHs and PCBs was investigated in three matrices (dissolved phase, associated to SSM and sediment). Fifteen stations located in six rivers at the cross-border area of northern France and Belgium were studied. Their distribution in dissolved, particulate and sedimentary phases depended strongly on their physicochemical properties. Low molecular weight PAHs were mainly present in dissolved phase while HMW-PAHs accumulated preferentially in SSM and sediments. For PCBs, PCB153 congener remain detectable even though PCBs use have been banned for many years; it was found mainly in sediment. The spatial distributions are also studied and a correlation between Σ_{16}PAHs and PCB153 concentrations was observed. Various types of combustion such as wood and coal burning and vehicular emissions could be the major sources of the contaminations for the studied sites. Industrial and domestic activities could be the major sources of these contaminations for the studied sites. Industrial and domestic activities could be major contributors. The most polluted sampling stations are generally closed to big cities. Moreover, high levels of nitrate indicate that agriculture may be a non-negligible source of pollution. Considering ecotoxicological assessment, based on PCB153, the sampling sites were identified at good quality. However, PAHs and 2-methylphenanthrene are likely to adversely affect aquatic wildlife.

Acknowledgment

The authors are gratefully indebted to the Nord-Pas-de-Calais Region, Foundation for Biodiversity Research (FRB) and the Water Agency (Artois Picardie) for their financial support for this work in BIOFOZI project. The authors would like to thank Romain Descamps and ECOLAB Laboratory for all the technical support and assistance during sampling campaign. We thank the associate editor and the anonymous reviewers for improving the quality of the manuscript.

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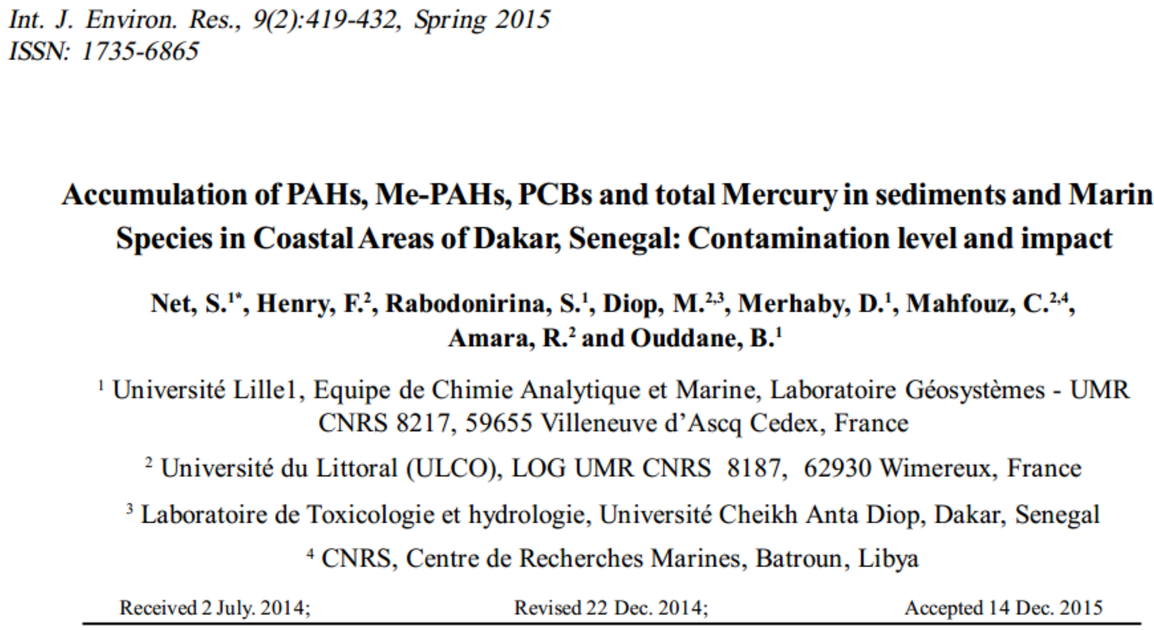
Article 2

Accumulation of PAHs, Me-PAHs, PCBs and total Mercury in sediments and Marine Species in Coastal Areas of Dakar, Senegal: Contamination level and impact.



Int. J. Environ. Res., 9(2):419-432, Spring 2015
ISSN: 1735-6865

Accumulation of PAHs, Me-PAHs, PCBs and total Mercury in sediments and Marine Species in Coastal Areas of Dakar, Senegal: Contamination level and impact

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Received 2 July. 2014; Revised 22 Dec. 2014; Accepted 14 Dec. 2015

ABSTRACT

Persistent organic pollutants (POPs) have widely aroused public concern due to their ubiquity, environmental persistence, long-range transportability, bioaccumulation capacities and potentially adverse effects on living organisms. Dakar is located in the industrial zone of Senegal (80% of industrial activities) and inhabits 25% of Senegalese population leading to an ideal sink of these persistent organic pollutants. In the present paper, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) were analyzed in sediments and marine organisms. The contamination level of PAHs, Me-PAHs and PCBs in surface sediment and aquatic organisms (one macroalgae, two invertebrate species, four fish species and macroalgae) were determined. The concentration levels in the sediment were detected from 2 to 636 µg/kg dw for Σ_{16}PAHs, from 3 to 31 µg/kg dw for Σ_{18}Me-PAHs and from 4 to 333 µg/kg dw for Σ_{28}PCBs for the selected stations in Dakar costal area. PAHs concentrations determined in edible tissues were lower than sediment samples. Tilapia species present the highest mean levels of PAHs and Me-PAHs at 92 ± 54 and 183 ± 39 µg/kg dw respectively. For PCBs, the highest level was determined in *Perna perna* species (up to 1228 µg/kg dw) and the lowest level was found in *Penaeus kerathurus* species. At the base of the food chain, *Ulvalactula* species displayed low PCB concentrations detected at 7 ± 6 µg/kg dw. The total mercury concentration was also reported in this paper in order to complete the background of pollution degree and to study the potential processes of biomagnification and/or bioaccumulation of contaminants in marine food chain. Mercury concentration were detected in the sediment ranging from 5 to 95 µg/kg dw. For marine species, considering all organisms, the mean concentration of mercury varies between 5 and 442 µg/kg dw. Pyrogenic process was the predominant source of PAHs contamination in our sampling sites. Based on Sediments Quality Guidelines (ERM–ERL/TEL–PEL approaches) rare biological adverse effects of total mercury, PCBs and PAHs on aquatic ecosystems were expected in Dakar costal area. Finally, in the context of human health, the edible marine species qualities obtained from three stations of Dakar coastal areas have been also evaluated. Based on the European Union legislation, the selected species present good quality for human consumption based on PCBs, PAHs and mercury.

Keywords: PAHs, PCBs, mercury, sediment and marine organisms, Dakar.

INTRODUCTION

The environmental impact of organic pollutants and metallic trace elements in coastal environment is serious. In order to better understand the potential impact of these pollutants on the ecosystem functioning as well as human health, an increasing attention has been implemented not only on the contamination level of contaminants in water or sediment but also on their accumulation level in aquatic organism (Boon, 1985; Naes et al., 1995; Neff 2002; Borgå et al., 2004; Francioni, 2005; Bastami et al., 2013). Senegalese coast is one of the most productive areas in the world due to the presence of coastal upwelling of deep waters rich in nutrients (Romeo et al., 1999). Even if industrialization did not reach a very high level compared to the developed countries, pollution of coastal aquatic habitats seems to be an inevitable problem mainly in the peninsula of Dakar which concentrates more than 80 % of the industries and inhabits more than 25 % of the population of the country (OIS 2010). Indeed, most of domestic and industrial waste waters are discharged directly into the sea. These permanent anthropogenic discharges can contribute to environmental and ecological degradation of Dakar coastal zones. Consequently, particular attention must be paid to the chemical quality of edible marine organisms consumed by local human populations. Fish and invertebrates consumption remain the major source of protein for the residents in Dakar. However, to date, only few studies were carried out on the trace metals and organic contamination levels in mollusk and fish species sampled from this aquatic ecosystem (Simoudou et al., 2006; Ndiaye et al., 2012). Among the large variety of organic pollutants, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are two classes of pollutants intensively monitored and regulated due to their toxicity, persistence and wide diffusion in the environment. PCBs were widely used in industries until their hazards to the environment and human health became evident. These contaminants have been reported to cause cancer in animals and humans (Bertrand et al., 2010; Kramer et al., 2012; Bräuner et al., 2012; EPA, 2013). PCBs have primarily been used as dielectric fluids of transformers and capacitors; other applications included their use in paints, inks and pesticides; they are extremely stable compounds under environmental conditions (Bennett, 1983; WHO, 1993). Due to their toxicity, persistency and bioaccumulation capacities, these substances have been classified as persistent organic pollutants. Their production was banned by the United States Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants in 2001 (Porta and Zumeta, 2002). However, PCBs are still present in water and sediment (Turrio-Baldassarri et al., 2005; Dumoulin et al., 2013; Net et al., 2014a) and continue to affect aquatic organisms from the base of food chain (plankton, algae) to predator organisms (fish, birds, marine mammals) and consequently human health through the diet (Sun et al., 2002). Another class of organic contaminants is represented by the aromatic hydrocarbons group including PAHs and Me-PAHs. These contaminants are widely disseminated in the environment. High level of hydrocarbons represents a serious threat to the ecosystem functioning and human health via food chain and water resources. Their sources can be both natural and anthropogenic (Yunker et al., 2002; Wang et al., 2007; Mostert et al., 2010; Net et al., 2014a,b). Hydrocarbons are highly lipophilic compounds, ubiquitous in coastal, estuarine and river water column, as well as sediments in which they tend to accumulate (Chiou et al., 1998; Ko and Baker, 1995; Manodori et al., 2006; Cailleaud et al., 2007; Gaspare et al., 2009; Yunker et al., 2012; Net et al., 2014b). Recent studies have reported that marine organisms are prone to bioaccumulate these substances, particularly in lipid-rich tissues (Neff, 2002; Francioni et al., 2005; Dugan et al., 2005). Due to their toxic, carcinogenic and mutagenic effects (Straif et al., 2005; IARC, 2010; US Department of Health and Human Services, 2011), sixteen PAHs have been classified as priority substances by the United States Environmental Protection Agency (US EPA, 2002). Among toxic metals, mercury is an element of special concern because it is known to particularly biomagnify as it moves up the aquatic food chain (Carrasco et al., 2011) and thus to bioaccumulate in higher tropic level consumers (Cossa et al., 1990).

The aim of the present study was to assess the impact of anthropogenic discharges on the ecological ecosystem of Dakar coastal zones. Predominant organic compound (PCBs, PAHs and Me-PAHs) were quantified in one macro algae species (*Ulvalactuca*), two invertebrate species (mussel: *Perna perna* and shrimp: *Penaeus kerathurus*) and four fish species (grey mullets: *Mugilcephalus*, tilapia *Sarotherodon melanotheron*, flatfish *Soleasenegalensis* and round sardinella *Sardinella aurita*). These two invertebrate and four fish species have been selected because they represent a great economic and ecological importance in these coastal zones. In addition, a toxic metal such as mercury has been also considered in this paper in order to complete the background of contamination level and to study their potential biomagnification and/or bioaccumulation processes in marine food chain.

MATERIALS AND METHODS

Dakar is located in the west of Senegal, in the industrial zone (80% of industrial activities) and inhabits 25% of the Senegalese population which is an ideal sink of these persistent organic pollutants. The sampling campaign was conducted in the south of Dakar on February 2013 during dry season in three sampling sites along the South coast of the peninsula of Dakar, noted A, B and C on the Fig. 1. Classical parameter such as pH, temperature, salinity and dissolved oxygen have been also measured simultaneously. The values of pH, temperature, salinity and dissolved oxygen were respectively at 7.43, 21.8°C, 36.9 PSU and 7.42 mg/L for Soumbedioune station, 7.61, 23.4°C, 40.3 PSU and 6.19 mg/L for Yarakh station and 7.64, 23.1°C, 35.8 PSU and 7.02 mg/L for Rufisque station.

Surface sediment and marine species have been selected in order to understand the potential impact of micro pollutants from urban and industrial discharges on ecosystem functioning and on human health. Seven marine species were considered in this work starting from macroalgae, bivalve, crustacean and four species of fish. The choice was based on the frequent consumption of these species by the population inhabiting the Senegalese coast. The main characteristics of marine organisms selected in this study are briefly presented as following: (i) Macroalgae: *Ulvalactuca* provide qualitative information about the contamination level and environmental quality in an ecosystem due to their lifestyle sedentary and abundance in coastal seawater (Rainbow and Phillips, 1993). (ii) Mussel: *Perna perna* is the only mussel of this genus in the Western coast of Africa (Sidoumou et al., 2006). Mussels are sedentary filtering organisms, which have been widely used as environmental sentinel for the contamination. (iii) Crustacean: *Penaeus kerathurus* is commercially one of the most important shrimp species in fishery in Senegal. It is also a target species for fishermen using trammel nets in Dakar bays. (iv) Fish species: *Sardinella aurita* is a small pelagic fish feeding on plankton. These fat fish are the more often consumed species in Senegal. In this study, *Sardinella aurita* presents from 228 to 337 cm length with mean average of 309±37 cm and from 110 to 396 g with mean average of 304±91 g wet weight. *Flathead mullet Mugilcephalus* is cosmopolitan and occupies a wide variety of marine, estuarine and freshwater environment in tropical, subtropical and temperate coastal waters. This benthopelagic species is omnivorous which diet consists mainly of zooplankton, benthic organisms and detritus for larger juveniles and adult stages. In this word, *Mugilcephalus* collected were from 318 to 362 cm length with mean average of 343±19 cm and from 282 to 426 g wet weight with mean average of 334±57 g wet weight. *Sarotheroron melanotheron:* As Mugilcephalus, Sarotheroron melanotheron are tolerant to a broad range of environmental conditions and natural populations were found in many different habitats from freshwater to hypersaline waters (Panfili et al., 2003). This species has an omnivorous diet and can change its diet in function of the environment. Tilapia is a fast-growing fish which has been an essential source of protein food. Therefore, this fish species show an increasing demand in many developed countries. *Sarotheroron melanotheron* collected were from 141 to 253 cm length with mean average of 196±58 cm and from 85 to 342 g with mean average of 206 ± 129 g wet weight. *Soleasenegalensis* is one of the most abundant and representative species of the Atlantic coasts. This flat benthic fish with a practically sedentary life lives in sandy or muddy bottoms in coastal areas and feeds on benthic invertebrates such as larvae of polychaets, bivalve mollusks and small crustaceans. This species is well adapted to warm climates and have been used in field and laboratory toxicity assays because of its sensitive character to pollutants (Costa et al., 2009). *Soleasenegalensis* collected were from 269 to 371 cm length with mean average of 311±40 cm and from 178 to 445 g with mean average of 279 ± 97 g wet weight.

These three sampling sites were chosen due to their locations near the waste discharge channels into the sea. Zone A (Soumbedioune) is dominated by discharges of domestic wastewater, hospital discharges and road traffics. Zones B (Yarakh) and C (Rufisque) are located in the Hann Bay: Yarakh is surrounded with industrial activities with the predominance of food industries while Rufisque is close to the Refining African society and cement factory. For each station, five superficial sediment samples were collected at low tide. Similarly, macroalgae and mussels were handpicked from substratum of intertidal zone. After collection, samples were transported to the laboratory in icebox and biota samples were rinsed with pure water. The whole soft body of mussels was collected for chemical analysis. Samples of fish and shrimp were caught by fishermen’s nets and the fishing zones were indicated approximately in the fig. 1. Species were purchased from the local fishermen in the same day of capture and brought to laboratory on ice immediately. Before collecting muscle tissues, fish length and weight were measured. All samples were dried in an oven at 40°C to constant weight and were stored in individual aluminum foils at -20°C until further treatments and analysis. Dried sediment and biota samples were ground mechanically with an agate mortar and manually with a ceramic mortar and pestle, respectively.

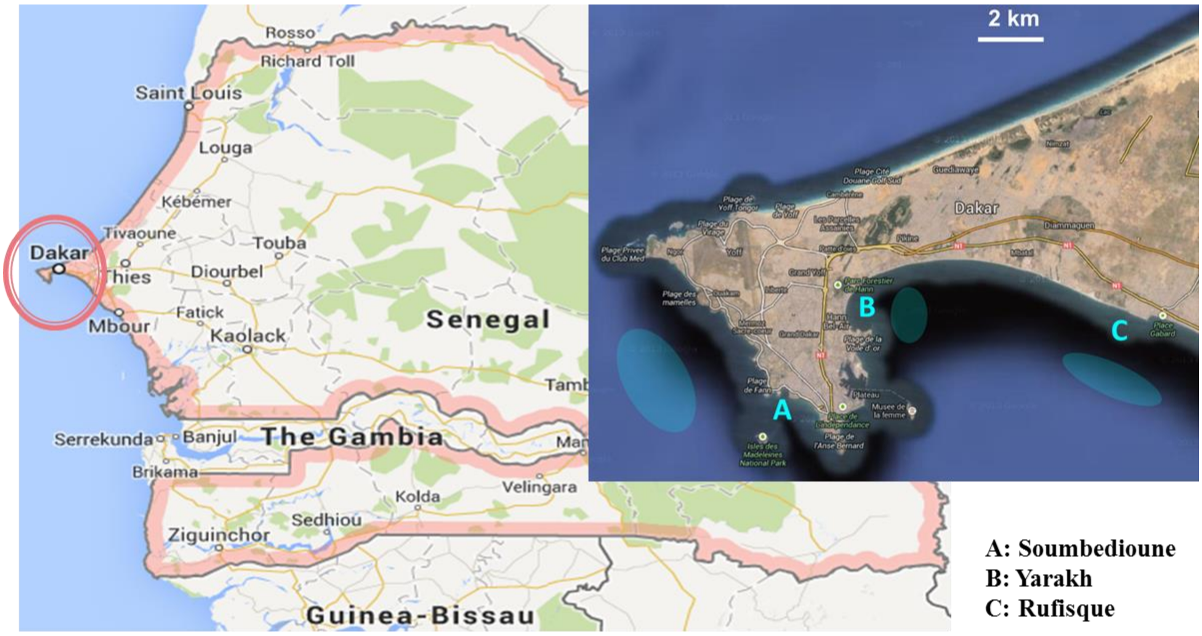

Fig. 1. Location of sampling sites from Dakar coastal zone, in Senegal.

Mixed standard solutions of PAHs and Me-PAHs were purchased from Restek Corp (Bellefonte, PA, USA). PCBs standard solution was obtained from Accustandard, Inc. (New Haven, CT, USA). Tetrachloronaphtalene (TCN), 2,3,3',5,6-tetrachlorobiphenyl (PCB112) and octachloronaphtalene (OCN), used as internal standard for PCBs quantification, were purchased from Dr Ehrenstorfer (Augsburg, Germany). Deuterated internal standards for PAHs and Me-PAHs quantification were acenaphthene-d10 (A-d10), naphtalene-d8 (N-d8), perylene-d12 (Per-d12), phenanthrene-d10 (Phe-d10) and pyrene-d10 (Pyr-d10) and they were provided by LGC-Promochem (Middlesex, UK). HPLC-grade solvents (hexane, dichloromethane, methanol and acetone) were purchased from Dislab (France). Ultrapure water (Milli-Q) was produced by a Millipore apparatus with 18.2 MΩ/cm resistivity. Merck silica gel 60 (70-230 mesh ASTM) activated at 450 °C was stored at 120°C for 12h prior to use. Glassware was systematically washed with detergent (Decon, East Sussex, UK), rinsed with ultrapure water and acetone and finally dried at 120 °C prior to use.

In this work, 16 PAHs, 18 Me-PAHs and 28 PCBs including 12 dioxin-like PCBs (dl-PCBs) and 7 PCB indicators (PCBi) were analyzed as follow:

PAHs (16 PAHs) : naphthalene (N), acenaphtylene (Acy), acenaphtene (Acn), fluorene (F), anthracene (An), fluoranthene (Fl), benzo*[a]*anthracene (BaA), chrysene (Chr), benzo*[a]*pyrene (BaP), phenanthrene (Pn), benzo*[b]*fluoranthene (BbF), benzo*[k]*fluoranthene

(BkF), benzo*[ghi]*perylene (Bghi), dibenzo*[a,h]*anthracene (DhA), indeno*[1,2,3-cd]*pyrene (IP), pyrene (Py).

Me-PAHs (18 Me-PAHs) : 1-methylnaphthalene (1M-Na), 2-methylnaphthalene (2M-Na), 1,2-dimethylnaphthalene (1,2DM-Na), 1,6-dimethylnaphthalene (1,6DM-Na), 2,6-dimethylnaphtalene (2,6DM-Na), 1-methylphenanthrene (1M-Pn), 2-methylphenanthrene (2M-Pn), 3-methylphenanthrene (3M-Pn), 9-methylphenanthrene (9M-Pn), 2-methylanthracene (2M-An), 1,7-dimethylphenanthrene (1,7DM-Pn), retene, 1-methylfluoranthene (1M-Fl), 3-methylfluoranthene (3M-Fl), 1-methylpyrene (1M-Py), 4-methylpyrene (4M-Py), 3-methylchrysene (3M-Ch), 6-methylchrysene (6M-Ch).

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

Mercury: Total mercury.

PAHs, Me-PAHs and PCBs determination: Sieved powder samples were spiked with deuterated internal standards A-d10, N-d10, Per-d12, Phe-d10 and Pyr-d10 for PAHs and Me-PAHs analyses and with TCN, PCB112 and OCN for PCBs analysis. After a delay of equilibration, samples were then extracted using an accelerated solvent extraction (ASE 200, Dionex Corp., USA). The extraction conditions were: heat 5 min, temperature 100°C, static solvent extraction time 2 min with 5 static cycles, pressure 138 bars, purge 3 min and 35 % flush according to the method developed by Tronczynski et al. (2005). High purity nitrogen was employed as the purge gas.

Molecular sulfur was removed from the extract by addition of activated metallic copper (Blumer, 1997) to the extracts. The extracts were concentrated, solvent-exchanged to hexane, and then purified and fractioned by liquid chromatography on a silica column to eliminate organic interferences (Jeanneau, 2007). PCBs were recovered by elution with hexane (Fraction 1), and aromatic hydrocarbons (PAHs and Me-PAHs) were recovered with hexane/dichloromethane mixtures (3/1 *v/v*) followed by hexane/dichloromethane mixture (1/1 *v/v*) (Fraction 2). Each fraction was concentrated using a rotary evaporator followed by a slight stream of nitrogen to a final volume of 200µL.

Targeted compounds were analyzed using a Varian 3900 gas chromatograph (GC) equipped with a deactivated fused-silica guard column (5 m, 0.25 mm i.d.) and a fused-silica low polarity si-arylene ZB-XLB capillary column (60 m length, 0.25 mm i.d., 0.25 µm film thickness, Phenomenex) and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS). The carrier gas was helium held at a constant flow rate of 1 mL/min. Each group of organic compounds was analyzed separately. Temperature of the GC oven was programmed as follow: from 70 °C (1 min) to 170 °C at 10 °C/min, then to 230 °C at 4 °C/min, and then to 300 °C at 3 °C/min (13 min) for HAPs and Me-HAPs and from 80 °C (1 min) to 170 °C at 10 °C/min, then to 230 °C at 4 °C/min, and then to 300 °C at 3 °C/min (19 min) for PCBs. Samples were injected in the splitless mode at 280 °C and the injector was purged with helium after 1 min. The transfer line and the ion trap were held at 280 °C and 220 °C, respectively. Identification of each compound was done on the basis of the retention time and the mass spectrum from chromatograph of standard solutions acquired in full scan mode. Quantification was then performed in the single ion storage (SIS) mode for better selectivity. Response factors were determined relative to the internal standards previously chosen to better fit to the properties of each compounds. No significant amount of analytes was detected in procedural blanks. Thus, the data did not need the blank corrected. The recovery rates of the analytical procedure for extraction of PAHs and PCBs have been previously studied and validated by Tronczynski et al. (2005). The procedure have been slightly modified for fractionation on a silica column step. The recovery rates have been studied and validated in the laboratory by spiking the targeted compounds into the natural sediment. The recovery rates obtained were more than 79% for PAHs, more than 73% for Me-PAHs and more than 75% for PCBs in algae and sediment samples. The limit of quantification of individual PCBs, PAHs and Me-PAHs were 0.8 µg/kg dw (except for PCB180 which was 2 µg/kg dw), 0.1-2 µg/kg dw and 0.2-0.4 µg/kg dw, respectively.

Mercury analyses: Total mercury analysis was carried out with an Advanced Mercury Analyser (Altec, AMA 254) on powder samples without treatment at least three replicates for each sample. For a known amount of dried sample (10-40 mg), the metal was evaporated by progressive heating up to 800 °C under oxygen atmosphere and finally amalgamated on a gold-sand trap. Afterwards, the amalgamator was heated to liberate the collected mercury, which was finally measured by atomic absorption spectrophotometry. Certified reference materials (MESS-3 and DORM-3, National Research Council Canada) were used to assess the accuracy and precision of the analyses. Mean recovery for total mercury was more than 86 % and the limit of quantification was 5 µg/kg dried weight (dw).

RESULTS AND DISCUSSIONS

The mean contaminant levels of total mercury, total PAHs (Σ_{16}PAHs), total Me-PAHs (Σ_{18}Me-PAHs) and total PCBs (Σ_{28}PCBs) measured in surface sediment were at 22±22 µg/kg dw with the range of 5-95 (n=15), 197±240 with the range of 2-636 (n=15), 11±8 with the rage of 3-31 (n=15) and 58±81 µg/kg dw with the range of 4-333 µg/kg dw (n=15) respectively. Mean ± S.D (standard deviation) of individual concentration of targeted compounds were presented in Table 1. Individual concentration of PAH and Me-PAH detected in Soumbedioune station were one order of magnitude lower compared to previous study reported by Ndiaye et al. (2012) for the same station. Individual concentration of PCB were also detected at lower concentration. However, there is no data on organic contamination reported for two other sites selected in this study. Among these three sampling sites, Yarakh was the less contaminated by PAHs and PCBs. Our results showed that the distribution of PAH, Me-PAH, PCB and mercury was not homogenous. The concentration varied strongly form one sampling point or site to another (Table 1). Despite a large range between the minimum and maximum for contaminant levels, Σ_{16}PAHs showed a relatively high contamination level, around 9 times higher than mercury concentration, 3 times higher than Σ_{28}PCBs concentration and 18 times higher than Σ_{18}Me-PAHs concentration.

Table 1: Means ± S.D of individual concentration of targeted compounds (16PAHs, 18Me-PAHs, 28PCBs and total mercury) analyzed in sediment and marine organisms collected from three sampling stations in the Dakar coastal area: invertebrate species (soft body*)* and fish species (muscle). *nd* = level not detected (<LOQ) and *na* = not analysis. (n ≥3 replicate).

Compounds	**Maximum admissible content (µg/kg wet weight)**			
	Mussel	**Fish**	**Crustacean**	**Reference**
BaP, BaA, BbF, Chr	30	30^{*}	30^{*}	UE N° 835/2011
	3.4-20 (8)	0.2-4.3 (1.1)^{1} 8 – 34(19)^{2} 3.2-18 (10.1)^{3} 1.8-3.2 (2.7)^{4}	8-12 (10)	This work
PCB: 28, 52, 101, 138, 153, 180	75	75	75	UE N° 1259/2011
	0.7-12 (6)	n.d-12 (5)^{1} n.d^{2} 7-10 (8.5)^{3} n.d-27 (6)^{4}	nd	This work
Total mercury	100-500	500-1000	100-500	UE N° 466/2001/2006
	9-17 (12)	3-101 (34)^{1} 11-38 (21)^{2} 9-30 (22)^{3} 4-18 (7)^{4}	7-12 (9)	This work

The PAHs ranged between 2 and 636 µg/kg dw and the highest PAHs concentrations were obtained in sediments collected at Rufisque station and sampled from a zone close to the Refining African society and cement factory. The mean concentration of Σ_{16}PAHs was 396 ± 326µg/kg dw (Fig. 2). Our results of PAHs was at least an order of mag nitude lower, compared to concentrations measured in superficial sediment collected in the Soumbedioune station (Hann Bay) during the dry season (Ndiaye et al., 2012). Abdolahpur Monikh et al. (2014) have performed the study on PAHs contamination in Persian Gulf. The authors have reported the concentrations of total PAHs in sediment varied from 310.76 µg/kg dw at Boshehr province to 1106 µg/kg dw at Tangestan estuary; thus two order of magnitude higher than our results obtained from Dakar coastal. Ndiaye et al. (2012) reported a concentration level of 19 µg/kg dw for PCBs indicator in a sediment sample from Hann Bay. The levels of PCBs indicator (Σ_7PCBs) were similar in Rufisque station and lower than literature data for the two other stations (Fig. 2). Similarly, surface sediments from two Senegalese stations (100 – 150 km South from Dakar) exhibited Σ_7PCB concentrations ranging between 0.3 and 19.1 µg/kg dw (Bodin et al., 2011). Sediments from Yarakh and Soumbedioune displayed levels of POPs lower than those from Rufisque station (Fig. 2). Yarakh station seems to be the less contaminated compared to other ones. The location of Rufisque station near the Refining African society and cement factory could explain the highest level of organic pollutants found at this station and more particularly the PAH compounds. Mercury concentrations ranged between 5 and 95 µg/kg dw and sediments from Rufisque station were the less enriched in this element. To our knowledge, no data for mercury concentration in sediments from this area or along the Senegalese coast were reported.

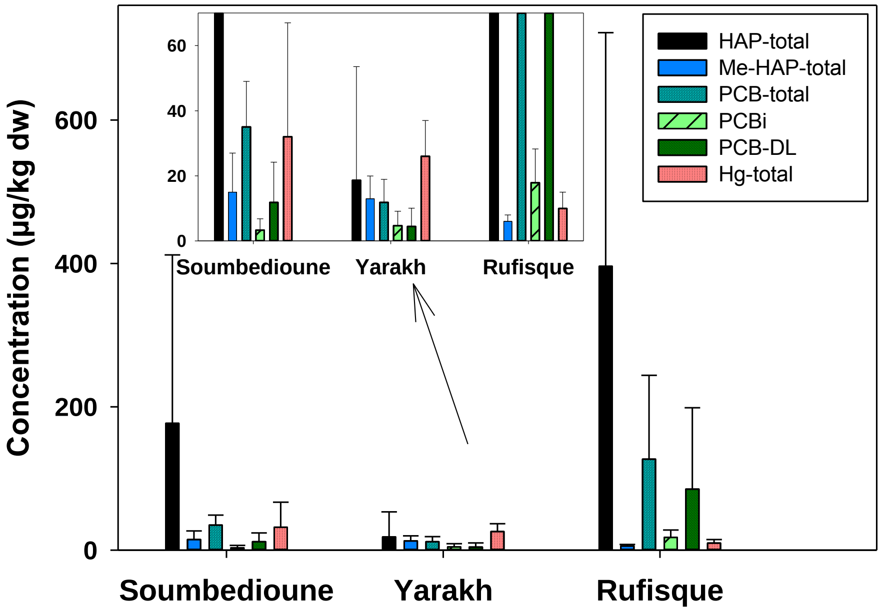

Fig. 2: Mean (±S.D.) of total PAH, Me-PAH, PCB and mercury concentrations (µg/kg dw) obtained in surface sediments collected at Soumbedioune, Yarakh and Rufisque stations. Levels of PCB indicators (PCBi) and dioxin-like PCBs (PCB-DL) are also indicated. n=five replicates.

In general, the contamination level of pollutions are strongly conditioned by their origin. Numerous methods could be used to identify the origin of PAHs contaminations (De Lucas 2005; Gogou et al., 1996; Simo et al., 1997; Yunker et al., 2002; Yunker and Macdonald, 1995; Dickhut et al., 2000; Zhang et al., 2005). However, to our knowledge, there is no specific method to identify the origin of PCBs and mercury. In this work, PAHs origin for the sediment samples was characterized by using the ratio of low molecular weight and high molecular weight (LMW/HMW, the sum of (2-3) / (4-6) aromatic rings). This ratios allow to distinguish the petrogenic (LMW/HMW > 1) from pyrolytic origins (LMW/HMW < 1) (De Lucas, 2005). Our results on LMW/HMW ratios revealed values less than 1, thus suggesting that combustion should be the dominant source of PAHs in the studied areas. In addition, ratios of molecular masses 178 and 228 are commonly used to distinguish combustion from petroleum sources. For the mass 178, Ant/(Ant + Phe) <0.10 suggests pollution of petroleum origin, while a ratio >0.10 indicates a dominance of combustion (Budzinski et al., 1997; Yunker et al., 2002; Liu et al., 2008). For the mass 228, BaA/ (BaA + Ch) suggests that a ratio <0.20 indicates petroleum inputs, a ratio between 0.20 and 0.35 indicates a mixed sources (either petroleum or combustion), and a ratio >0.35 indicates combustion sources (Yunker et al., 2002). Our results obtained from isomers ratios of molecular masses 178 and 228 reinforce the combustion process as the major source of PAHs contamination in these three sampling sites. Moreover, such high Ant/(Ant+Phe) and BaA/(BaA+Ch) ratios involve high proportions of anthracene and benz*[a]*anthracene that are both among the most photoreactive PAHs (Gogou et al., 1996). Considering a combustion/transport/deposition process, it can be admitted that no significant photolysis degradation occurred in this case study. These ratios can also imply close contamination sources that can be attributed to the nearby industrial activities or vehicle emissions of Dakar city.

However, there is no natural source of PCBs. Atmospheric depositions, runoff from the land, wood burning and food chain transport have been regarded as the major sources of PCBs in aquatic environment (Totten et al., 2006). PCBs are mainly produced by pyrogenic process due to the combustion of organic matter (Pereira et al., 1980; Kjeller and Rappe, 1995; Rose and Rippey, 2002; Rose et al., 2004; Pandelova et al., 2009). PCBs detected in Dakar coastal area could be originated from unintentionally atmospheric deposition, released from equipment, generators, ships, vehicles and trucks exhaust in the surrounding zone but the their origin could not be determined.

Similarly, the specific origin of mercury could not identified. It is a global pollutant that is ubiquitous in the environment from both natural and anthropogenic sources reaching the ocean through river inputs and atmospheric deposition (Fitzgerald et al., 2007). However, given their relatively low concentration of mercury detected, the domestic and industrial wastes discharged directly into Dakar Bay have not yet produced environmental mercury contamination in this coastal zone. Contrarily, two other toxic metals such as cadmium and lead present at high concentrations level in sediment of Dakar coastal (Diop et al., 2012).

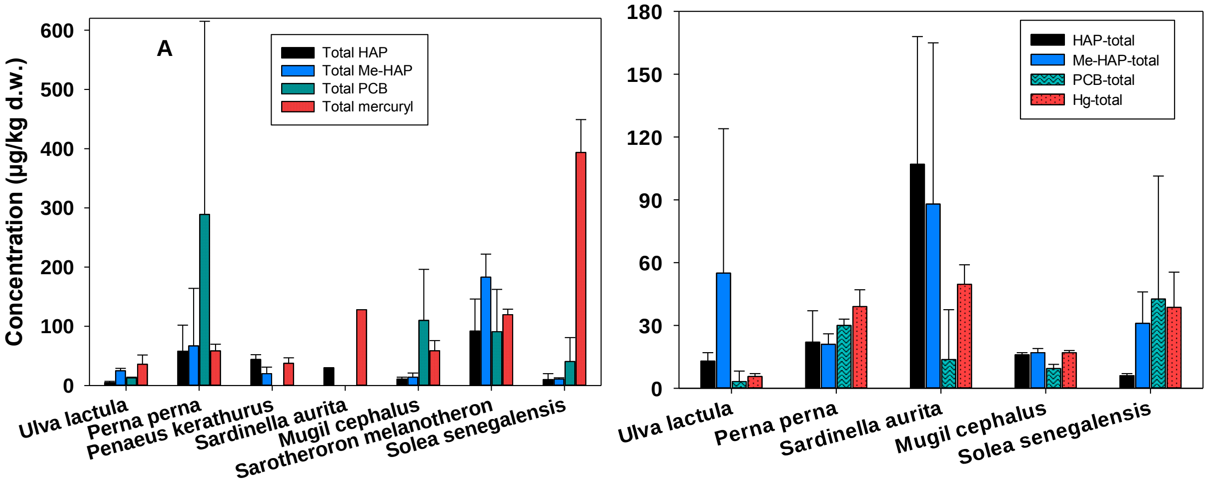

Fig. 3: Mean (±S.D.) concentrations of total PCBs, PAHs, Me-PAHs and Hg in biota samples: A) Soumbedioune station and B) Rufisque station.

For the ecotoxicological risk assessment, concentrations of total PCBs or Σ_{28}PCBs, sum of 12 PAHs or Σ_{12}PAHs (Aen, Ayl, An, F, N, Pn, BaA, BaP, Ch, DhA, Fl, Py) and total mercury were calculated. The mean concentrations of Σ_{12}PAHs were 279 (6 - 507), 119 (2 - 298) and 18 (1.2 - 80) µg/kg dw for Rufisque, Soumbedioune and Yarakh respectively. While Σ_{28}PCBs mean concentrations detected in the sediments from Rufisque, Soumbedioune and Yarakh were 127 (57 - 332), 34 (16 - 47) and 12 (4 - 22) µg/kg dw respectively. Total mercury concentrations did not exceed 95 µg/kg dw. Total mercury, Σ_{12}PAHs and Σ_{28}PCBs concentrations were compared to Sediment Quality Guidelines (SQGs) which provide a valuable tool to evaluate the potential biological adverse effect on aquatic organism caused by contaminated sediments (Long et al. 1995). The ERL/ERM (Effect range low/Effect range median) developed by Long and Morgan (1990) and the TEL/PEL (threshold effect level/Probable effect level) developed by Macdonald et al., (1996) are two based approaches which can be used to assess the ecological toxicity of total PAHs and PCBs concentrations (Σ_{12}PAHs and Σ_{28}PCBs) in sediments collected from Dakar coastal in Senegal. According to SQGs, the classification of biological adverse effects are rarely expected (<ERL/TEL) with minimal-effects range, occasionally (≥ERL/TEL and <ERM/PEL) with possible-effects range, and frequently (≥ERM/PEL) with a probable-effects range (Long et al., 1995; Cardellicchio et al., 2007). TEL-PEL values were 655-6676 and 22-189 µg/kg dw for the ΣPAHs and ΣPCB, respectively (Macdonald et al., 1996). While ERL-ERM were 4022-44792, 23-180 and 150-710 µg/kg dw for the ΣPAHs, ΣPCBs and mercury, respectively (Long and Morgan, 1990). Our results showed that Dakar coastal sediments have rarely to occasionally biological adverse effects for mercury, PCBs and PAHs in Dakar aquatic ecosystems.

Overall, even if there is a strong influence of urban and industrial activities in this coastal zone, sediment contamination by PAHs, Me-PAHs, PCBs, and mercury were detected at moderate levels. This is probably due to the tide which is responsible to the rapid renewal of sea water, therefore sedimentation processes are not preferred. Indeed, the coastline around Dakar is called microtidal, the tidal range which varies between 0.5 m (neap period) and 1.6 m (during spring tides) (Ruffman et al., 1977). This suggests that urban and industrial waste discharged into Dakar coastal zones could be diluted or transported rapidly seaward.

Due to their high toxicity, persistency and bioaccumulation capacities, the concentration of these contaminants have been also studied in marine organism in order to evaluate the quality of edible species. Mean ±S.D of individual concentration of PAH, Me-PAH and PCB and mercury determined in biota samples from all sampling stations of the Dakar coastal area are shown in Table 1. Comparisons of targeted compounds were significantly different between the stations and between species. Considering all organisms, the mean concentration of mercury varies between 5 and 442 µg/kg dw. Generally, muscle tissues of fishes exhibited the highest concentrations of Hg compared to macroalgae and invertebrate species. The highest levels of mercury were detected in *Soleasenegalensis* from Soumbedioune station (Fig. 3). Mercury levels measured in *Sardinella aurita* were in the same order of magnitude compared to the mean concentration values reported for the same species collected along the coast of Mauritania in a previous study at 90 ± 80 µg/kg dw (Romeo et al., 1999).

For PCBs concentrations, the highest level was determined in *Perna perna* species (up to 1228 µg/kg dw) and the lowest level was found in *Penaeus kerathurus* species. At the base of the food chain, *Ulvalactula* species displayed low PCB concentrations (7 ± 6 µg/kg dw) while fish species exhibited mean values ranging between 10 ± 20 µg/kg dw for *Sardinella aurita* and 95 ± 32 µg/kg dw for *Sarotheroron melanotheron*. Except for *Perna perna*, *Penaeus kerathurus* and *Sardinella aurita*, PCB concentrations were in the same range between organisms and sediments while mercury concentrations were higher in biota than sediment samples. Whereas, PAH concentrations determined in edible tissues were lower than sediment samples. This may be due to a rapid transformation of PAHs into more hydrophilic metabolites. Therefore, marine organisms exposed to these compounds indicate only trace quantities of PAHs in their tissues (Vuorinen et al., 2006). The concentration level in marine organisms varied from species to species (Table 1 and Figure 3). This may be translated by behavioral patterns of organisms such as feeding habit, the rate of movement and reproduction status (Vuorinen et al., 2006).

The highest mean levels of PAHs and Me-PAHs (92 ± 54 and 183 ± 39 µg/kg dw respectively) were detected in the tilapia species, therefore the present study supports the idea to use this species as a sentinel in order to monitor chemical pollutants (Ndiaye et al., 2012; Harrison and Whitfield, 2006). Our results showed moderate accumulations of PAHs and Me-PAHs in *Mugilcephalus* and *Soleasenegalensis*. For these two families of organic compounds, similar concentrations were determined in biota samples collected from Soumbedioune and Rufisque stations (Fig. 3). Rose et al. (2012) have reported the concentration of ΣPAHs in Tilapia guineensis obtained from Lagos Lagoon of Nigeria at the same order level of 62.24 µg/kg dw. This result were the same order of magnitude as the concentration of ΣPAHs in Tilapia obtained in our study. Compared to other species of fish, Mullus barbatus and Serranus cabrilla collected from Tarragona of Mediterranean accumulated ΣPAHs at the levels of 164.9 and 62.9 µg/kg dw respectively (Escartin and Porte, 1999). Amodio-Cocchieri et al., (1993) reported the concentration of ΣPAHs in Engralis enchrasicholus collected from the Bay of Naples of Italy at the level of 965 µg/kg dw. The highest concentration in fish have reported by McGill et al. (1987) in Limanda limanda collected from the British North Sea at the level of 2345 µg/kg dw. This concentration was much higher than ΣPAHs concentration detected in four species selected in our study. More recently, Abdolahpur Monikh et al. (2014) have also reported the concentration of PAHs in benthic, benthopelagic and pelagic fish species from the Persian Gulf much higher than our results.

Σ_{16}PAHs concentrations detected in targeted species were lower compared to concentrations in sediment. However, Σ_{16}PAHs concentrations were detected in all marine species selected in this work. ΣMe-PAHs was present at low levels in the sediment samples (Fig. 2). However, their concentrations were detected at higher levels in most of marine species (Table 1; Figure 3). The results clearly showed that all species does not have the same affinity to each type of contaminant.

Generally, we observed the bioaccumulation of these contaminants in marine species. However, the bioaccumulation level varies strongly from one species to another (Table 1; Fig. 3). Each species accumulates at least two types of pollutants. Among targeted species, both *Sarotheroron melanotheron* and *Perna perna* accumulated all type of contaminants (PAHs, Me-PAHs, PCBs and mercury). The contamination level of PCBs in *Sarinella aurita* and *Penaeus Kerathurus* were under the detection limits (Fig. 3). For Yarakh station, all targeted compounds were quantified in the sediments. However, only mercury was quantified in marine species. For marine species collected in Yarakh site, high levels of mercury were detected in *Sardinella aurita* (71.6±23.3 µg/kg dw) and *Sarotheroron melanotheron* (71.3±28.0 µg/kg dw). *Ulvalactula, Mugilcephalus, Perna perna, Penaeus Kerathurus* and *Solea senegalensis* species accumulated levels of total mercury at 40.7±5.6, 21.7±6.0, 49.0, 31.0, 15.7±3.0 µg/kg dw respectively.

To estimate the potential public health risks, the European Union legislation has established maximum allowed levels in aquatic products for different toxic compounds including some PAHs, PCBs and mercury (Table 2). PAHs, PCBs and mercury concentrations obtained in dry weight (µg/kg dw) were converted into µg/kg wet weight (w.w.) in order to compare with the guideline values. According to the weighed mass before and after drying, the following factors were applied to obtain the concentrations in wet weight: 0.23 for muscle of *Mugilcephalus*, *Sarotherodon melanotheron*, *Solea senegalensis* and edible tissue of *Perna perna*, 0.30 for muscle of *Sardinella aurita* and 0.26 for *Penaeus kerathurus.*

Two limit values are listed for mercury depending on the type of mussel and fish (Table 2). For all species, mercury and PCBs levels do not show concentrations exceeding limits fixed by the European Union. In addition, the levels of these compounds in the investigated area were low compared with these threshold values. Concerning PAHs, the proposed limit values are for smoked products of fish and crustacean species because recently the European legislation (Official Journal of the European Union, 2011) abrogated the limit of PAHs in these fresh seafood because it has been shown that PAHs are quickly metabolized in these species (Storelli et al., 2013). In our study, limit level (30 µg/kg wet weight) was exceeded only in a *Sardinella aurita* sample with a muscle tissue concentration of 34 µg/kg wet weight. Based on European legislation, the selected species present good quality for food based on PCBs, PAHs and mercury.

Table 2: Σ_4PAHs, Σ_6PCBs and total mercury detected in this work (range and mean values into brackets) compared to maximum admissible content expressed in μg/kg wet weight. n.d. = not detectable (<LOQ).

Compound	**Sediment**	***Ulvalactula*** **(green algae)**	***Perna perna*** **(mussel, mollusks)**	***Penaeus kerathurus*** **(shrimp, crustaceans)**	***Sardinella aurita*** **(sardine, pelagicfish)**	***Mugilcephalus*** **(mullet, bentho-pelagic fish)**	***Sarotheroron melanotheron*** **(tilapia, bentho-pelagic fish)**	***Soleasenegalensis*** **(sole, benthic fish)**
Soumbedioune								
PAHs (μg/kg dw)								
N	3.4±6.3	nd	nd	nd	nd	nd	nd	nd
Acy	6.7±8.9	0.5±0.0	1.9±1.4	1.9±0.3	1.3	0.5±0.3	6.5±0.9	0.8±0.1
Acn	nd		nd	nd	nd	nd	nd	nd
F	4.2±5.7	0.4±0.2	1.5±2.0	0.3±0.2	0.9	nd	1.1±0.3	nd
An	25.7±35.1		1.4±2.8	0.2±0.4	nd	nd	1.5±1.8	nd
Fl	3.2±7.1	0.5±0.7	3.7±5.7	nd	nd	nd	8.9±8.4	nd
BaA	63.3±86.8	0.3±0.0	22.7±9.2	35.2±6.1	24.2	9.6±3.5	4.7±2.2	6.3±9.6
Chr	6.4±12.9	0.3±0.0	5.4±4.7	4.3±0.7	2.9	1.2±0.4	6.9±3.1	1.3±0.9
BaP	nd	nd	nd	nd	nd	nd	nd	nd
Pn	1.6±3.6	1.8±0.6	3.1±1.7	0.2±0.2	nd	nd	5.4±5.1	nd
BbF	33.7±35.5	0.3±0.0	11.6±16.7	nd	nd	nd	32.2±28.1	0.3±0.2
BkF	24.5±33.4	0.3±0.0	1.5±3.3	nd	nd	nd	11.8±15.0	0.3±0.2
Bghi	nd	nd	nd	nd	nd	nd	nd	nd
DhA	nd	nd	nd	nd	nd	nd	nd	nd
IP	nd	nd	nd	nd	nd	nd	nd	nd
Py	4.5±5.5	0.9±0.6	5.6±7.4	1.6±0.2	0.7	0.3±0.1	13.1±4.2	0.6±0.3
Me-PAHs (μg/kg dw)								
1M-Na	2.9±2.6	3.9±3.6	6.9±6.3	17.6±9.1	nd	4.0±5.7	28.2±31.9	nd
2M-Na	1.0±1.1	2.8±3.0	3.1±5.2	4.1±7.7	nd	0.1±0.1	38.4±30.7	nd
1,2-DM-Na	2.4±1.7	4.4±4.0	9.6±3.5	17.6±8.7	nd	6.2±1.9	27.5±31.0	9.5±1.2
1,6-DM-Na	2.7±2.0	5.8±6.8	7.1±11.4	8.4±17.3	nd	0.7±0.3	84.7±69.4	0.6±0.3
2,6DM-Na	0.9±1.0	1.2±0.0	1.6±1.1	0.6±1.0	nd	0.4±0.5	4.7±2.2	0.7±0.4
1M-Pn	nd	0.7±0.2	nd	nd	nd	nd	nd	nd
2M-Pn	1.2±2.7	1.8±0.5	nd	nd	nd	nd	nd	nd
3M-Pn	nd	2.1±0.4	nd	nd	nd	nd	nd	nd
9M-Pn+2Me-An	1.4±3.1	1.3±0.6	nd	nd	nd	nd	nd	nd
1,7DM-Pn	1.7±3.8	0.9±1.3	nd	nd	nd	nd	nd	nd

Retene	0.8±1.8	nd	11.9±22.7	1.6±1.0	nd	nd	nd	nd
1M-Fl	nd	nd	1.2±2.7	nd	nd	nd	nd	nd
3M-Fl	nd	nd	5.5±12.3	nd	nd	nd	nd	nd
1M-Py	nd	nd	6.6±14.7	nd	nd	nd	nd	nd
4M-Py	nd	nd	3.6±8.2	nd	nd	nd	nd	nd
3M-Ch	nd	nd	3.9±8.6	nd	nd	nd	nd	nd
6M-Ch	nd	nd	6.1±13.5	nd	nd	nd	nd	nd
PCBs n° (µg/kg dw)								
8	8.1±5.3	4.1±1.2	nd	nd	nd	nd	nd	nd
18	3.4±5.7	nd	nd	nd	nd	nd	nd	nd
28	0.8±1.2	0.9±0.2	nd	nd	nd	nd	5.5±5.5	nd
44	nd	nd	0.9±1.1	nd	nd	nd	1.6±2.7	0.9±1.0
52	nd	nd	7.4±7.6	nd	nd	nd	2.0±3.5	nd
66	6.4±14.1	nd	4.1±6.1	nd	nd	nd	nd	2.3±4.0
77	nd	nd	42.4±94.8	nd	nd	nd	nd	15.0±18.2
81	nd	nd	nd	nd	nd	nd	nd	nd
101	nd	nd	14.4±21.9	nd	nd	4.7±6.7	12.5±12.4	0.8±1.4
105	2.7±3.5	nd	nd	nd	nd	nd	nd	nd
114	nd	nd	88.3±197.4	nd	nd	13.3±5.4	44.3±76.7	nd
118	1.2±2.4	nd	5.6±8.0	nd	nd	nd	nd	nd
123	2.5±5.3	nd	nd	nd	nd	nd	nd	nd
126	nd	nd	nd	nd	nd	nd	nd	nd
128	nd	nd	nd	nd	nd	nd	nd	nd
138	0.8±1.5	4.0±1.1	54.4±116.8	nd	nd	35.3±42.8	nd	8.8±7.6
153	1.4±0.6	nd	42.1±61.1	nd	nd	27.0±19.3	7.7±13.4	1.0±8.5
156	nd	nd	nd	nd	nd	nd	nd	nd
157	nd	nd	nd	nd	nd	nd	nd	nd
167	nd	nd	nd	nd	nd	nd	nd	nd
169	nd	nd	nd	nd	nd	nd	nd	nd
170	nd	nd	23.7±37.5	nd	nd	2.4±3.3	nd	4.5±4.1
180	nd	nd	5.7±5.5	nd	nd	24.3±19.3	nd	nd
187	nd	nd	nd	nd	nd	nd	nd	nd
189	2.7±6.0	nd	nd	nd	nd	nd	nd	nd
195	2.3±4.2	4.1±0.7	nd	nd	nd	2.9±4.1	17.0±29.5	3.2±5.4
206	nd	nd	nd	nd	nd	nd	nd	nd
209	nd	nd	nd	nd	nd	nd	nd	nd
Total mercury (µg/kg dw)								

Mecury	32.0±35.0	36.0±15.0	58.8±11.3	37.6±9.2	128.0±0.0	58.7±17.1	119.7±9.3	393.7±55.5

Compound	**Sediment**	***Ulvalactula*** **(green algae)**	**Perna perna (mussel, mollusks)**	***Penaeus kerathurus*** **(shrimp, crustaceans)**	***Sardinella aurita*** **(sardine, pelagicfish)**	***Mugilcephalus*** **(mullet, bentho-pelagic fish)**	***Sarotheroron melanotheron*** **(tilapia, bentho-pelagic fish)**	***Soleasenegalensis*** **(sole, benthic fish)**
Rufisque								
PAHs (µg/kg dw)								
N	2.8±1.7	nd	nd	na	nd	nd	na	nd
Acy	10.9±8.8	0.4±0.1	0.7±0.1	na	3.7±1.6	0.4±0.4	na	1.3±0.0
Acn	nd	nd	nd	na	nd	nd	na	nd
F	7.6±6.1	0.3±0.1	0.3±0.2	na	1.9±2.2	0.3±0.1	na	0.1±0.0
An	76.2±76.3	0.1±0.2	2.1±0.1	na	9.6±6.2	0.5±0.7	na	0.7±1.1
Fl	1.4±1.9	0.4±0.7	0.9±0.6	na	3.1±5.3	nd	na	nd
BaA	117.0±95.0	7.2±2.2	13.3±1.3	na	68.0±30.2	11.3±1.2	na	0.8±0.2
Chr	0.1±0.2	0.9±0.3	1.6±0.4	na	8.3±3.7	1.4±0.1	na	0.8±0.2
BaP	nd	nd	nd	na	nd	nd	na	nd
Pn	83.3±186.3	2.2±0.6	2.9±1.5	na	7.6±7.6	1.5±1.5	na	nd
BbF	68.9±46.3	nd	nd	na	nd	nd	na	0.7±0.0
BkF	47.9±32.2	1.0±1.8	nd	na	nd	nd	na	0.7±0.0
Bghi	nd	nd	nd	na	nd	nd	na	nd
DhA	nd	nd	nd	na	nd	nd	na	nd
IP	nd	nd	nd	na	nd	nd	na	nd
Py	3.6±3.1	1.0±0.7	0.4±0.1	na	5.1±5.7	0.6±0.2	na	1.1±0.2
Me-PAHs (µg/kg dw)								
1M-Na	2.2±1.3	7.2±7.5	8.6±0.8	na	35.9±43.3	7.5±0.4	na	10.8±6.9
2M-Na	0.1±0.1	2.9±2.5	0.4±0.2	na	12.9±12.7	0.4±0.1	na	4.3±6.6
1,2-DM-Na	2.4±1.4	35.4±5.5	8.0±0.9	na	33.8±40.3	7.2±0.5	na	5.8±7.0
1,6-DM-Na	0.2±0.2	6.8±5.6	2.1±0.5	na	26.6±32.5	0.5±0.1	na	9.2±15.3
2,6DM-Na	nd	2.5±2.2	1.4±0.3	na	5.4±0.3	0.8±0.3	na	0.6±0.7
1M-Pn	nd	nd	nd	na	3.6±5.0	nd	na	nd
2M-Pn	nd	nd	nd	na	5.0±7.1	nd	na	nd
3M-Pn	nd	nd	nd	na	6.8±9.6	nd	na	nd
9M-Pn+2Me-An	nd	nd	nd	na	nd	nd	na	nd
Retene	nd	nd	nd	na	nd	nd	na	nd
1,7DM-Pn	0.6±1.4	0.2±0.4	nd	na	nd	nd	na	nd
1M-Fl	0.1±0.1	nd	nd	na	2.4±3.4	nd	na	nd

3M-Fl	nd	nd	nd	na	nd	nd	na	nd
1M-Py	nd	nd	nd	na	nd	nd	na	nd
4M-Py	0.1±0.1	nd	nd	na	nd	nd	na	nd
3M-Ch	nd	nd	nd	na	nd	0.7±1.2	na	nd
6M-Ch	nd	nd	nd	na	nd	0.4±0.6	na	nd
PCBs N° (µg/kg dw)								
8	15.8±9.3	nd	nd	na	nd	nd	na	nd
18	1.5±2.9	nd	nd	na	nd	nd	na	nd
28	2.0±2.3	nd	nd	na	nd	nd	na	0.8±1.1
44	nd	nd	nd	na	nd	nd	na	nd
52	nd	nd	nd	na	nd	0.9±0.9	na	nd
66	nd	nd	nd	na	nd	nd	na	nd
77	nd	4.4±6.2	nd	na	nd	nd	na	nd
81	nd	nd	nd	na	nd	nd	na	nd
101	5.3±6.0	nd	nd	na	nd	1.0±0.9	na	1.5±1.9
105	5.5±9.2	nd	nd	na	nd	1.1±1.9	na	nd
114	3.4±5.5	0.8±0.6	6.8±9.6	na	nd	nd	na	nd
118	3.2±3.0	nd	nd	na	nd	nd	na	nd
123	2.0±1.3	nd	nd	na	nd	nd	na	nd
126	4.9±8.2	nd	6.7±9.5	na	nd	nd	na	nd
128	1.0±2.1	nd	nd	na	nd	nd	na	nd
138	1.0±2.2	nd	nd	na	nd	3.4±0.7	na	10.8±16.3
153	0.2±0.3	nd	1.5±2.1	na	nd	3.4±1.2	na	3.8±5.4
156	nd	nd	nd	na	nd	nd	na	nd
157	2.4±5.4	nd	nd	na	nd	nd	na	nd
167	31.0±69.3	nd	nd	na	nd	nd	na	nd
169	nd	nd	nd	na	nd	nd	na	nd
170	1.0±1.4	nd	nd	na	nd	nd	na	1.7±2.6
180	6.3±11.6	nd	nd	na	nd	0.9±0.8	na	12.1±24.1
187	nd	nd	nd	na	nd	nd	na	nd
189	32.8±42.4	nd	nd	na	nd	nd	na	nd
195	7.6±11.0	nd	nd	na	13.7±23.8	nd	na	0.8±1.6
206	nd	nd	nd	na	nd	nd	na	nd
209	nd	nd	nd	na	nd	nd	na	nd
Total mercury (µg/kg dw)								
Mercury	10.0±5.0	5.6±1.4	39.0±8.0	na	49.7±9.3	17.0±1.0	na	38.7±16.8

Compound	**Sediment**	***Ulvalactula* (green algae)**	**Perna perna (mussel, mollusks)**	***Penaeus kerathurus* (shrimp, crustaceans)**	***Sardinella aurita* (sardine, pelagicfish)**	***Mugilcephalus* (mullet, bentho-pelagic fish)**	***Sarotheroron melanotheron* (tilapia, bentho-pelagic fish)**	***Soleasenegalensis* (sole, benthic fish)**
Yarakh								
PAHs (µg/kg dw)								
N	nd	na	na	na	na	na	na	na
Acy	0.2±0.0	na	na	na	na	na	na	na
Acn	1.2±1.8	na	na	na	na	na	na	na
F	nd	na	na	na	na	na	na	na
An	nd	na	na	na	na	na	na	na
Fl	5.38±11.7	na	na	na	na	na	na	na
BaA	1.3±2.6	na	na	na	na	na	na	na
Chr	1.7±2.5	na	na	na	na	na	na	na
BaP	nd	na	na	na	na	na	na	na
Pn	0.9±0.8	na	na	na	na	na	na	na
BbF	0.7±1.0	na	na	na	na	na	na	na
BkF	nd	na	na	na	na	na	na	na
Bghi	nd	na	na	na	na	na	na	na
DhA	nd	na	na	na	na	na	na	na
IP	nd	na	na	na	na	na	na	na
Py	6.8±14.2	na	na	na	na	na	na	na
Me-PAHs (µg/kg dw)								
1M-Na	1.7±1.4	na	na	na	na	na	na	na
2M-Na	0.9±1.4	na	na	na	na	na	na	na
1,2-DM-Na	1.7±1.1	na	na	na	na	na	na	na
1,6-DM-Na	3.1±2.7	na	na	na	na	na	na	na
2,6DM-Na	0.7±0.9	na	na	na	na	na	na	na
1M-Pn	0.6±1.2	na	na	na	na	na	na	na
2M-Pn	0.2±0.2	na	na	na	na	na	na	na
3M-Pn	0.4±0.6	na	na	na	na	na	na	na
9M-Pn+2Me-An	1.7±1.6	na	na	na	na	na	na	na
Retene	nd	na	na	na	na	na	na	na
1,7DM-Pn	nd	na	na	na	na	na	na	na
1M-Fl	nd	na	na	na	na	na	na	na
3M-Fl	nd	na	na	na	na	na	na	na
1M-Py	1.4±3.1	na	na	na	na	na	na	na

4M-Py	0.3±1.0	na	na	na	na	na	na	na
3M-Ch	nd	na	na	na	na	na	na	na
6M-Ch	nd	na	na	na	na	na	na	na
PCBs n° (µg/kg dw)								
8	2.4±5.4	na	na	na	na	na	na	na
18	0.8±0.5	na	na	na	na	na	na	na
28	nd	na	na	na	na	na	na	na
44	nd	na	na	na	na	na	na	na
52	nd	na	na	na	na	na	na	na
66	nd	na	na	na	na	na	na	na
77	3.2±3.6	na	na	na	na	na	na	na
81	nd	na	na	na	na	na	na	na
101	1.6±1.8	na	na	na	na	na	na	na
105	nd	na	na	na	na	na	na	na
114	nd	na	na	na	na	na	na	na
118	1.0±2.2	na	na	na	na	na	na	na
123	nd	na	na	na	na	na	na	na
126	nd	na	na	na	na	na	na	na
128	nd	na	na	na	na	na	na	na
138	0.9±0.9	na	na	na	na	na	na	na
153	1.5±1.3	na	na	na	na	na	na	na
156	nd	na	na	na	na	na	na	na
157	nd	na	na	na	na	na	na	na
167	nd	na	na	na	na	na	na	na
169	nd	na	na	na	na	na	na	na
170	0.8±0.7	na	na	na	na	na	na	na
180	nd	na	na	na	na	na	na	na
187	nd	na	na	na	na	na	na	na
189	nd	na	na	na	na	na	na	na
195	nd	na	na	na	na	na	na	na
206	nd	na	na	na	na	na	na	na
209	nd	na	na	na	na	na	na	na
Total mercury (µg/kg dw)								
Mercury	26.0±11.0	40.7±5.6	49.0±0.0	31.0±0.0	71.6±23.3	21.7±6.0	71.3±28.0	15.7±3.0

Conclusion

Our study provide a data base about the organic contamination levels of PCBs, PAHs, Me-PAHs and total mercury in sediments and marine organisms obtained from Dakar coastal zone. The distributions of PAHs and Me-PAHs suggested that their sources were mainly originated from pyrolytic origin of nearby activities. The evaluation of ecotoxicological risk based on SQGs suggested that the biological adverse effects of PAHs, PCBs and total mercury are expected from rarely to occasionally for marine organisms. However, even if the impact of this type of pollution is moderate, it is now urgent to adopt adequate pollution control strategies into this coastal area before the problem become irreversible given the high density of population in this zone and continuous discharges of domestic and industrial effluents for most case without any treatment. Indeed, most of domestic and industrial waste waters are rejected directly into the sea and these permanent anthropogenic discharges can produce environmental and ecological degradation in the coastal zones. Moreover, the tide is quiet important in this coastal zone leading to a significant transport process of pollutants out to the sea. Particular attention must be paid to the chemical levels in edible marine organisms consumed by local population. Fish and invertebrates consumption remain the major source of protein for the residents in Dakar area. The result on the contamination level of PCBs, PAHs, Me-PAHs and total mercury in marine comestible species showed rarely to occasionally impact on aquatic organisms and no significant impact on human health by consuming targeted species namely mussel, crustacean, sole, sardine, tilapia, and mullet sampled from these coastal areas of Dakar. However, given the only few data available on the degree of contamination levels in these marine species and before making any final conclusion, it is strongly recommended to carry out complementary studies on these comestible species and others.

ACKNOLEDGMENT

The authors are gratefully indebted to the IREPSE (Institut de Recherches Pluridisciplinaires en Sciences de l'Environnement) of Université Lille 1 for its financial support.

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