Contamination Des Calanques Par Les Micropolluants Organiques (Cortiou), Zone Côtière De Marseille, France

Organic micro-pollutant contamination in Calanques (Cortiou Creek), coastal area of Marseilles, France

THÈSE
Présentée à
Aix-Marseille Université
École doctorale des Sciences de l'Environnement
Laboratoire Chimie Environnement

Pour obtenir le grade de
DOCTEUR
Spécialité : Chimie de l'environnement

Par
Halikuddin UMASANGAJI

Soutenue publiquement le mercredi ***19 décembre 2018*** *à 10 h00*
Lieu : Salle Amphitéatre du CEREGE Europole de l'Arbôis, Aix-en-Provence

Composition du jury

Pr Abdellatif BOUKIR	Université Sidi Mohammed Ben Abdellah - Faculté des Science et Techniques Fès – Département de Chimie	Rapporteur
Pr Syafsir AKHLUS	Université Maritim Raja Ali Haji – UMRAH (Recteur)	Rapporteur
Dr Aurore ZALOUK - VERGNOUX	Université de Nantes – Faculté de Pharmacie – Département 1 – Chimie Générale, Minérale et Analytique	Examinateur
Dr Laurence ASIA	Aix – Marseille Université – CNRS - Département de Chimie	Examinateur
Pr Henri WORTHAM	Aix – Marseille Université – CNRS - Département de Chimie	Examinateur Président du jury
Dr Agung Dhamar SYAKTI	Universitas Jenderal Soedirman (UNSOED) Marine and Fisheries Faculty	Co-Directeur de thèse
Pr Pierre DOUMENQ	Aix – Marseille Université – CNRS - Département de Chimie	Directeur de thèse

Contamination des calanques par les micropolluants organiques (Cortiou), zone côtière de Marseille, France

Résumé

L'explosion démographique mondiale a entraîné une augmentation massive des apports de contaminants environnementaux anthropiques, par ex. les hydrocarbures pétroliers, les pesticides, les biphényles polychlorés (PCBs) ainsi que d'autres déchets domestiques tels que les détergents utilisés comme nettoyants ménagers. En raison de leur persistance et du fait de leur toxicité, les résidus de ces contaminants organiques, qui peuvent être détectés dans les différentes matrices environnementales (eau, sédiments, air et biote), parfois à très faible concentration (micropolluants), ont gagné l'attention du public. Face à un tel risque, il est désormais nécessaire d'évaluer l'impact environnemental de ces contaminants à travers des programmes de suivi. Dans la zone étudiée (Parc National des calanques Calanques, Cortiou), ces micropolluants atteignent l'environnement marin, à la fois via l'émissaire de la station d'épuration (STEP) de l'agglomération de Marseille ou sont directement déversés dans les bassins versants, les rivières et la mer. Cette étude vise à déterminer les niveaux de concentration des contaminants sélectionnés dans les sédiments marins de surface et à identifier les sources. Les micropolluants organiques ciblés sont classés comme polluants organiques persistants (POP), à savoir les hydrocarbures aromatiques polycycliques (HAPs), les alkylbenzènes linéaires (LABs), les pesticides organochlorés (OC), les polychlorobiphényles (PCBs) et les alkylphénols (APs). De plus, nous avons évalué les effets potentiels de ces polluants sur les organismes benthiques à l'aide de plusieurs indices éco-toxicologiques. Les résultats de l'étude ont montré que la zone de Cortiou est fortement contaminée par les hydrocarbures. Les indices basés sur les abondances relatives d'hydrocarbures montrent que les intrants biogéniques terrestres sont la principale source de n-alcanes. La contribution anthropique reste néanmoins très significative (utilisation des hydrocarbures fossiles, activités maritimes). Par contre, les sources pyrolytiques dérivées de la combustion du bois et de la biomasse contribuent majoritairement aux HAP dans les sédiments de surface. Les rapports I/E mesurés sur les LAB ont des valeurs faibles, ce qui peut être interprété comme le résultat de rejets d'eaux usées insuffisamment traitées. De plus, de faibles rapports I/E ainsi que de fortes concentrations sédimentaires pour les C_{13}-LAB et les 6-C_{12}-LAB peut être le reflet de processus de biodégradation dans le sédiment et d'un apport chronique important d'eaux usées incomplètement traitées. Concernant les PCB et les OC, vu les teneurs sédimentaires et les toxicités développées, la comparaison avec les valeurs guide des sédiments (RQS) disponibles démontre des effets négatifs probables pour les sédiments et les biotopes marins et plus particulièrement au niveau des communautés benthiques, et ce pour une bonne partie des stations. Dans ce travail, nous avons également trouvé des alkylphénols (AP) en fortes concentrations dans les sédiments, les sols et des aérosols prélevés à proximité de l'exutoire des eaux usées. Ces composés ont été probablement été émis par l'exutoire et présentent des origines multiples (principalement domestiques et industrielles). En conclusion, Cortiou et ses environs sont fortement touchés par les contaminants anthropiques. Des programmes de surveillance à long terme sont nécessaires pour évaluer les effets de la réglementation actuelle et future, afin de mieux suivre la restauration de cette importante zone côtière marine située au «coeur» du parc marin national des Calanques.

Organic micro-pollutant contamination in Calanques (Cortiou Creek), coastal area of Marseille, France

Abstract

Demographic explosion has led to increase intensively environmental contaminants issued from different anthropogenic release e.g. petroleum hydrocarbons, pesticides, polychlorinated biphenyls (PCBs) and also other domestic waste such as detergents as household cleaner. Due to their persistence and the toxicological point of view, the remnants of these organic contaminants, which can be detected in the different environmental matrices (water, sediment, air and biota), sometimes with very low concentration (micropollutants), has gained the public attention. Facing such a risk, it is now necessary to assess the environmental impact through monitoring programs. In the studied area (Cortiou Creek), such micro-pollutants reach marine environment, both via wastewater treatment plant (WWTPs) from Marseille agglomeration and directly discharged into the watershed i.e. rivers, and to the sea. This study aims to determine the concentration levels of selected contaminants in surficial sediments and identifying the source of these chemicals in Cortiou Creek. The targeted organic micro-pollutants are categorized as persistent organic pollutants (POP's) namely polycyclic aromatic hydrocarbons (PAH), linear alkylbenzenes (LAB), organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs) and Alkylphenols (APs). Additionally, we assessed the potential effects of these pollutants toward benthic organisms through several eco-toxicological indexes. The results showed high contamination by hydrocarbons in the studied area. The calculated hydrocarbon indices suggest that terrestrial biogenic inputs are the main source of n-alkanes while pyrolytic sources derived from wood and biomass combustion contribute to the PAHs in surface sediments. According to I/E ratios related to LAB, we found the low values, that can imply an inadequately treated sewage discharge. More after, such low I/E ratios, as a result of high concentration of C13-LABs and 6-C_{12}-LABs in sediments, probably reflected that biodegradation processes occurred concomitantly with a chronic apportionment of untreated sewage loading. Concerning PCBs and OCs, through the comparison with available sediment quality guideline (SQG) values, the environmental significance and toxicological implications of PCBs and OCs reveal the probable adverse effects for the sediments and confirm an adverse effect for marine biota and more particularly for benthic communities for some stations. In this work, we also have found alkylphenols (APs) in high concentrations in sediments, soil and aerosols in the vicinity of the sewage outfall. These chemicals were supposed to be emitted by sewage outfall with multiple sources origins (mainly household waste and industrial activity). To conclude, Cortiou creek and surrounding areas are highly impacted by anthropic contaminants. Long-term monitoring programs are necessary to evaluate the effects of actual and future regulation, to better mitigate this important marine coastal area located in the "heart" of the National Marine Park of Calanques.

Contamination Des Calanques Par Les Micropolluants Organiques (Cortiou), Zone Côtière De Marseille, France

Sommaire

L'augmentation démographique au cours du siècle dernier est sans précédent. En cent ans, la population mondiale est passée de 1,7 milliard à 7,6 milliards. Ceci a entrainé de nouveaux besoins et a affecté considérablement les schémas de production et de consommation des produits chimiques et industriels (Ngô et Régent, 2012). Les conséquences nombreuses, ont notamment affecté le milieu marin (Ahmed et al 2017 ; Monaco et al 2017 ; Sarker et al 2018) et la santé d'humaine (Ke et al 2017 ; Tongo et al 2017 ; Wang et al 2017 ; Kadi et al 2018). Ces produits chimiques et industriels comprennent les micropolluants qui sont aussi bien organiques (Iwata et al 1994 ; Pereira et al 1994 ; Banjoo et Nelson 2005 ; de Mora et al 2005 ; Fung et al 2005 ; Numata et al 2005 ; Duodu et al 2017 ; Polidoro et al 2017) qu'inorganiques (Tranchida et al 2010 ; Marchand et al 2012 ; Yoo et al 2013 ; Harikrishnan et al 2017 ; Ashraf et al 2018 ; Naifar et al 2018) avec les éléments traces métalliques et métalloïdes (ETMM). Dans le cadre de ce travail, nous nous intéresserons aux micropolluants organiques.

Ces composés organiques, une fois répandus dans l'environnement, vont potentiellement l'impacter de façon variable selon leur mode d'émission, leur persistance et leur (bio)accumulation dans les compartiments ciblés. Parmi ces micropolluants organiques, nous nous sommes intéressés aux hydrocarbures aromatiques polycycliques (HAP), aux alkylbenzènes linéaires (LAB), aux pesticides organo-chlorés (OC), aux polychlorobiphényles (PCBs) et les certains polluants émergents notamment émis par les stations d'épuration (STEP) tels que les alkylphénols qui sont utilisés comme matières premières pour produire des alkylphénols éthoxylés (APEO) pour la fabrication de détergents et la préparation de résines phénoliques, polymères, stabilisants, antioxydants et agents de mûrissement (Duan et al 2014.) Ils pénètrent d'ailleurs principalement dans le milieu marin par les processus de biodégradation des APEO via l'eau rejetée traitée et non traitée (Chen et al 2005 ; Renner 1997 ; Liu et al 2016 ; Jeon et al 2017 ; Staniszwska et al 2017).

La plupart de ces produits sont aujourd'hui employés dans des secteurs divers, allant des usages domestiques aux usages industriels, ce qui peut induire leur accumulation non seulement dans l'environnement (Harman et al 2009 ; Duan et al 2014 ; Staniszewska et al 2015 ; Jeon et al 2017 ; Couderc et al 2016) mais aussi potentiellement au niveau des organismes (Cailleaud et al 2007 ; Couderc et al 2015 ; Staniszewska et al 2017 ; 2016 ; Ademollo et al 2017).

La présence des HAP dans l'environnement marin provient de deux sources principales : une source dite « pétrogénique » associés à des déversements de pétrole brut et de produits de raffinage (essences, kérosènes, gasoil, fuels…) (Duan et al 2018 ; Han et al 2018 ; Pongpiachan et al 2018 ; Perez-Umphrey et al 2018) et une source dite « pyrogénique » qui comprend des composés issues de la combustion des combustibles fossiles et de la biomasse, de l'incinération des déchets et de la production d'asphalte (Keshavarzifard et al 2017 ; Pokhrel et al 2017 ; Škrbić et al 2018). Ces hydrocarbures aromatiques sont ubiquistes dans l'environnement et attestent de la pression anthropique exercée sur les différents compartiments. A côté de cela, les alkylbenzènes linéaires (LAB) sont des marqueurs/indicateurs chimiques dérivés des détergents commerciaux qui sont contenus les effluents de traitement des eaux usées. Ils proviennent directement des activités domestiques, industrielles par la voie des eaux usées mais peuvent également avoir des voies de

transfert atmosphériques (Eganhouse et al 1988 ; Wang et al 2012 ; Zhang et al 2012 ; Wei et al 2014 ; Venturini et al 2015) Concernant les PCBs, ils sont considérés comme des polluants organiques persistants (POP) libérés dans l'environnement marin via les fleuves, le lessivage et les émissaires de STEP par l'industrie aussi bien qu'au niveau d'usages domestiques usages domestiques tels que dans les fluides échangeurs de chaleur, les transformateurs électriques et les condensateurs, comme additif dans les peintures, papiers autocopiants et plastiques. De fait ces derniers sont fréquemment découverts dans diverses matrices environnementales (Pan et al 2007 ; Okay et al 2009 ; Kampire et al 2015 ; Oziolor et al 2018) Enfin, les pesticides sont plus particulièrement transférés dans le milieu marin à partir des zones agricoles de par leur utilisation comme contrôle des ravageurs agricoles, au niveau des collectivités et particuliers dans les rejets urbains et d'autres industries. Bien que la plupart de ces composés chimiques soient maintenants très règlementés voire interdits, ils sont très fréquemment présents dans l'environnement marin (Alonso-Hernández et al 2015 ; El Nemr et El-Sadaawy 2016 ; Buah-Kwofie et Humphries 2017 ; Qu et al 2017 ; Dang et al 2018) et ce dans tous les compartiments.

Malgré les processus d'altération « naturels » que rencontrent ces composés lors de leur séjour dans l'environnement tels que l'évaporation, la dilution, la volatilisation et les phénomènes de dégradation par photo-oxydation et biodégradation, certains d'entre eux sont remarquablement récalcitrants. De fait, des concentrations parfois élevées de ces micropolluants organiques existent dans les différents compartiments environnementaux des zones marines proches de zones qui sont fortement urbanisés et industrialisés tel que le site d'étude que nous avons choisi.

UN grand nombre de travaux ont montré que ces substances posent problème non seulement pour la zone marine, mais aussi pour la santé humaine. Bon nombre de ces substances chimiques ont été classées mutagènes et cancérigènes (Li et al 2014 ; Yang et al 2015 ; Cetin et al 2018 ; Malarut et Vangnai 2018). Certains composés perturbent même le système endocrinien chez les humains et pour d'autres animaux (Annamalai et Namasivayam 2015 ; Grześkowiak et al 2016 ; Priac et al 2017 ; Balaguer et Bourguet 2018 ; Ramalho-Santos et Tavares 2018 ; He et al 2018 ; Vilela et al 2018). Cependant, à ce jour, ils sont encore découverts dans les aliments, le sang humain et l'urine (Ferrara et al 2011 ; Mezcua et al 2012 ; Sun et al 2012 ; Azzouz et al 2016 ; Shekhar et al 2017 ; Chung et al 2018). En raison de leur bioaccumulation et de leur toxicité envers l'environnement au sens large (biota), et les êtres humains (Çok et al 2012 ; García-Alvarez et al 2014 ; Luzardo et al 2014 ; Giuliani et al 2015 ; Saija et al 2016 ; Besis et al 2017 ; Kilonga et al 2017 ; Wang et al 2017), l'utilisation de ces substances a été interdite dans de nombreux pays du monde au travers des différentes réglementations/législations nationales.

Pour pouvoir décider de règlementer ces produits, il faut avoir une compréhension approfondie de leur devenir et de leurs effets dans les milieux étudiés. La Baie de Marseille, qui compte environ un million d'habitants, subit un fort impact urbain, industriel, portuaire et touristique. D'autre part, la création du parc national des Calanques en 2012, situé en périphérie sud-est de Marseille, est le premier parc national suburbain regroupant des écosystèmes terrestres et marins (environ 8300 hectares (terre) et 43.500 hectares (mer). En été, il y a plus de 1400 bateaux ancrés dans les calanques et ce site présente la particularité singulière d'accueillir les exutoires (émissaire de Cortiou) de la station de traitement des eaux usées de la Ville de Marseille et de 16 autres agglomérations (Asia 2012, thèse non-publiée) pour une charge de près de 1,7 millions d'équivalent-habitants. Cette situation plutôt paradoxale fait de cette zone un site d'étude extrêmement intéressant.

Dans ce contexte, le travail de thèse mis en place avait pour objectif de faire un état des lieux et d'avoir une meilleure compréhension de la contamination des sédiments marins de surface *directement en lien avec la STEP, en particulier aux niveaux de la Calanque de Cortiou, dans la baie de Marseille. Cette zone présente des caractéristiques particulières due à la sa situation géographique (typiquement méditerranéenne) et du nombre d'activités anthropiques (urbaines, industrielles et agricoles) dans ses bassins versants.*

Afin d'évaluer la concentration et le niveau de contamination, nous avons collecté 12 échantillons pour les HAP, les LAB, les PCB et les OC pesticides, et huit échantillons pour les AP. Nous avons également mené l'analyse du carbone organique total (COT). Après l'extraction des échantillons à l'aide de soxtherm et la purification en utilisant la chromatographie sur colonne, l'identification de ces produits chimiques par GC-MS et HPLC-PFD a été réalisée pour les HAPs et les LAB. L'analyse des AP, an été effectuée par GC-MS après dérivatisation (sylilation par BSTFA et TMCS). L'analyse de variance (ANOVA) et la régression linéaire ont été utilisées pour étudier les profils d'abondance des Σ n-alcane, ΣHAP et ΣLAB face aux propriétés physicochimiques (EOM, TC et TOC) dans les sédiments de surface de Cortiou et explorer les corrélations entre ces paramètres. Une valeur-p de 0,05 ou moins a été considérée comme significative pour tous les tests.

Cette étude visait à déterminer les sources et les niveaux de concentration de certains micropolluants organiques y compris les hydrocarbures aromatiques polycycliques (HAP), les alkylbenzènes linéaires (LAB), les polychlorobiphényles (PCB), les pesticides organochlorés (OC) et les alkylphénols (AP).

Le premier travail de cette thèse décrit les niveaux de concentration des n-alcanes, les HAP et leurs distributions spatiales à travers le panache de la STEP. Nous avons également tenté mettre en évidence leurs relations avec le carbone organique total (COT), qui joue un rôle majeur dans les processus d'adsorption des matières organiques. La distribution des n-alcanes aux 12 stations près de la STEP variait de 34,2 à 2155,8 $\mu g.kg^{-1}$ *avec une valeur moyenne de 941,25* $\mu g.kg^{-1}$*. Selon l'analyse statistique, nous avons trouvé qu'il y avait une faible corrélation positive entre les n-alcanes et le COT dans les stations majoritaires à l'exception des stations P7, P8 et P9, qui sont les plus proches de l'émissaire de la STEP. Ceci a permis de postuler que les n-alcanes sédimentaires de ces dernières stations provenaient de sources différentes de celles des autres stations. De plus, la majorité des stations à l'est de l'émissaire ont des concentrations plus élevées que les stations à l'ouest, ce qui a permis de proposer un taux de déviation moyen du panache de 85% vers la zone est.*

Par la suite, nous avons également caractérisé les sources et les origines de ces hydrocarbures en utilisant plusieurs indices diagnostiques de la littérature pour déterminer leurs origines soit pétrogénique ou pyrolytique. Parmi ces indices nous avons retenu les ***Σ*** *n-alcanes/C16, NAR, CPI, UCM/R, LMW/HMW (Discrimination entre biogénique et pétrogénique),Pr/Phy, n-C17/Phy, TAR, n-C29/n-C17. Comme aucun rapport n'est absolu nous avons analysé plusieurs indices pour avoir les interprétations les plus sures qui nous ont fourni dans la plupart des cas une origine mixte biogènique/pétrogénique/combustion. Bien que plusieurs indices aient donné une origine pétrogénique, la plupart des évaluations ont montré comme origine majoritaire le biogène du fait des apports de matière organique « terrestres » très importants via l'émissaire.*

En ce qui concerne les HAP nous avons mesuré des concentrations variant de 696,4 à 10699,4 $ng.g^{-1}$ *avec une valeur moyenne de 3620,8* $ng.g^{-1}$ *pour les 12 stations de notre site d'étude,. Ces valeurs sont inférieures aux concentrations obtenues par Pruell et Quinn en (1984) dans la baie de Naragawest, qui qui a des apports fluviaux, et sous l'influence d'activités urbaines et industrielles, allant de 20 à 1900* $\mu g.g^{-1}$ *et par les résultats de Naes et al (1995) en zone côtière norvégienne avec des ΣHAP* *allant de 135 - 310 $\mu g.g^{-1}$. Cependant, nos résultats sont plus élevés que ceux trouvés par (Zhang et al 2016 ; Xue et al 2016 ; Gu et al 2017 ; Hu et al 2017 ; Jeon et al 2017). De fait la revue bibliographique effectuée montre que de façon générale les concentrations en HAP dans les eaux ont diminué au cours des 3à dernières années. Le traitement statistique des données a montré que l'on pouvait positivement corréler les concentrations de HAP et de COT, sauf pour les stations P4 et P8, ce qui confirme que le COT joue un rôle important dans la sorption des hydrocarbures dans les sédiments de surface. Les concentrations les plus élevées ont été trouvées dans les stations P4 qui étaient plus proches de la station d'épuration et de la station P7 qui était au large. Ceci démontré qu'il n'y avait pas de piège spécial au niveau de la distribution des HAP. De plus, nous avons trouvé, comme pour les n-alcanes, qu'il y avait une augmentation des concentrations en HAP dans les stations situées à l'est de l'émissaire, Ceci est du à la direction générale du panache, majoritairement orienté vers l'est.*

Enfin les congénères de HAP dominants étaient respectivement le Fl, le B(a)Pyr, le B(a)Ant et le Chr.

La caractérisation des sources de HAP a été effectuée avec des indices d'abondance de congénères ou des ratio isomériques, tels que Phen/Ant, Fl/Pyr, Ant/$\Sigma 178$ bidimensionnel, Fl/$\Sigma 202$ et le diagramme en triangle proposé par Budzinski et al. (1997). Ce diagnostic a montré que les HAPs sur la surface des sédiments de Cortiou sont dérivés de sources mixtes à dominance soit pétrogénique, soit pyrolytiques. Enfin, concernant l'origine pyrolitique, elle est plutôt caractérisée par la combustion de la biomasse.

Afin d'être en mesure de donner une signification à ces valeurs de contamination, nous avons évalué les qualités sédimentaires de notre site d'étude en utilisant la notion d'ERL (Effects Ranges Low) et d'ERM (Effects Ranges Medium) proposé par Long et USEPA, 1995. Nous avons constaté que la majorité des stations ont été classées en dessous de l'ERL (4,02 $mg.kg^{-1}$) alors que les stations P4, P6 et P7 dépassent nettement ce seuil. Cela a montré que les sédiments de la plupart des stations n'étaient finalement que peu dangereux pour l'écosystème benthique., à l'exception des trois dernières stations.

Nous avons également pu mesurer les niveaux de concentrations des alkylbenzènes linéaires (LAB) les sédiments de surface de Cortiou. Les concentrations totales des congénères de LAB analysés dans les sédiments variaient de 43 à 502,3 $\mu g.kg^{-1}$ avec une valeur moyenne de 175,10 $\mu g.kg^{-1}$. Les composés prédominants étaient les 5-C_{12}, 4-C_{12}, 5-C_{11}, qui sont les plus utilisées dans les industries des détergents.

Ces résultats sont nettement inférieurs à ceux observés sur les sédiments par Chalaux et al (1992) de 421 $\mu g.g^{-1}$ sur la zone de l'effluent de l'usine de contrôle de la pollution des eaux du bassin de St Monica, Californie du Sud, États-Unis et ceux observés par Isobe et al 2004 en Asie du Sud et du Sud-Est (42,6 $mg.g^{-1}$). De plus, Dwiyitno et al (2015) Ont rapporté des valeurs de près de 330 $\mu g.g^{-1}$ pour les LABs dans les zones industrielles et urbaines de la baie de Jakarta, en Indonésie. On peut voir que dans les années 90 au début des années 2000, les concentrations de LAB ont subi une tendance qui a augmenté de manière significative. Cette forte concentration a été constatée dans les zones industrielles et urbaines de l'Asie du Sud et du Sud-Est, ce qui indique que eaux usées ont été déversées directement en mer ou que les traitements d'épuration n'ont pas été efficaces.

D'autre part, pour la plupart des stations, les résultats montrent une corrélation positive entre les concentrations mesurées sur les LAB et le COT. Ceci montre que le COT joue un rôle essentiel en termes de sorption de ces contaminants organiques dans les sédiments marins de surface. Enfin, nous *avons pu évaluer l'efficacité de la station d'épuration de la ville de Marseille par la quantification du rapport I/E de ces composés. En effet, ces rapports I/E ont démontré que le processus de biodégradation de ces molécules est largement incomplet. Si on prend en compte que la « tranche biologique » de la station Géolide, améliorant le fonctionnement de la station d'épuration a été installée 7 ans avant les prélèvements, cela prouve que les sédiments intègrent un signal d'au moins 7 ans. De fait, probablement du fait de la rémanence des profils « anciens de LABs, il n'est pas encore possible de conclure sur l'efficacité du nouveau traitement par l'amélioration du milieu.*

Dans la partie suivante de notre étude, nous avons détaillé l'occurrence de composés issus des activités de l'industrie agricole, des activités urbaines et industrielles. Ces sont les OCs pesticides et les PCBs. En ce qui concerne les OCs, nous avons pu déterminer la distribution spatiale de ces substances à travers le panache avec des concentrations qui varient entre 1.20 et 190.60 $\mu g.kg^{-1}$, pour une valeur moyenne cumulée de 89.58 $\mu g.kg^{-1}$. Les composés majoritaires étaient le pp'DDD et l'endosulfan sulfate. Ces résultats sont plus élevés que ceux rapportés par Kaljzic et al (1998) autour des zones urbaines et industrielles du lac de Simbirizzi, en Italie, ou pour la pollution ponctuelle et Cavanagh et al (1999) de la Grande Barrière de Corail, Queensland, Australie où ils sont liés aux activités agricoles Néanmoins, nos résultats sont beaucoup plus bas que ceux observés par Yu et al 2014 dans la zone agricole des sédiments de la rivière Chao en Chine. Ceci implique que ces OC sont encore utilisés dans plusieurs applications malgré la restriction d'usage depuis 1970, soit dans les industries, soit dans les activités agricoles notamment en Asie et en Amérique du Sud.

La distribution des OCs pesticides dans notre site d'étude a montré les plus fortes concentrations trouvées aux stations les plus proches d'émissaire de la STEP et a diminué modérément aux stations de P2 et P3. Néanmoins, ils ont augmenté aux stations P4 et P5. Ensuite, les niveaux des OCs pesticides ont été dilués dans les stations au large. Grâce à l'analyse statistique, contrairement aux HAPs et aux LABs, nous avons observé qu'il n'y avait pas de corrélation entre l'abondance des OCs et la présence de COT. Ceci implique qu'il y a d'autres facteurs qui contrôlent la sorption de ces substances dans les sédiments. Parmi ces facteurs, des facteurs locaux tels que les aspects météorologiques jouent probablement un rôle important dans ces processus. Enfin, les concentrations relevées sont plus élevées à l'est qu'à l'ouest du panache de dilution. Comme dit plus haut cette déviation du panache à l'est est due à l'influence du vent dominant. L'évaluation de la qualité des sédiments relativement aux OCs pesticides a permis de constater que certains sédiments de Cortiou sont probablement associés à des effets toxiques au niveau benthique.

Par la suite, nous avons présenté la distribution spatiale des PCBs sédimentaires au niveau du panache de dilution, près de l'émissaire de la STEP. Les concentrations rencontrées variaient entre 11.50 $\mu g.kg^{-1}$ et 791.50 $\mu g.kg^{-1}$ avec une valeur moyenne de 293.51 $\mu g.kg^{-1}$, avec pour congénères prédominants les CB-138 et CB-153. Ces résultats sont beaucoup plus faibles que ceux rapportés par Cordellicchio et al 2007 (ΣPCBs (2 - 1648 $\mu g.kg^{-1}$) qui était liée aux activités portuaires de la mer Ionienne, Italie du Sud, Fernandez et al 2000 (Σ PCBs 55.9 - 860 $\mu g.kg^{-1}$) en relation avec les zones urbaines, industrielles et agricoles du Parc Régional du Sud Est, Madrid, Espagne et Alegria et al (2016) (Σ PCBs 0.42 - 1232 $\mu g.kg^{-1}$) liés à la zone urbaine et industrielle. Cependant, ils sont plus élevés que ceux trouvés par Rizzi et al (2017) (ΣPCBs <DL - 5,87 $\mu g.kg^{-1}$) dans les zones industrielles et urbaines, Estuaire de la Baie de Babytonga, Brésil, Choi et al 2014 (ΣPCBs 1.08 – 3.5 $\mu g.kg^{-1}$) provenant de l'industrie, agriculture avancée, population élevée, Côte de Corée, Yu et al (2014) (ΣPCBs 0.0039 - 0,0365 $\mu g.kg^{-1}$) de la zone agricole du fleuve Chao, en Chine.

Dans cette étude, les concentrations des plus élevées ont été trouvées aux stations les plus proches de l'émissaire, à l'exception de la station P1. Ensuite les valeurs diminuent au centre du panache et réaugmentent au niveau des stations de large. Ceci pourrait être du à un transport relié au rayon hydrodynamique des particules de matière en suspension.–L'évaluation de la qualité des sédiments des stations de Cortiou, a montré que 50% d'entre elles étaient contaminés par des PCBs et celles qui restaient étaient fortement contaminées, en particulier P2, P3, P4, P5 près du point d'émissaire et P7, P8 qui sont nettement plus au large. Ces dernières stations

Finalement, nous nous sommes intéressés à la contamination de la zone côtière des Calanques de Cortiou par les alkylphénols qui sont des composés ayant une origine exclusivement anthropique et ont des propriétés de perturbateurs endocriniens. La distribution des AP étudiés (4-tert-OP, 4-n-OP et les trois isomères de nonylphénol NP_1, NP_2, NP_3) dans les sédiments des 8 stations directement en lien avec l'émissaire de la STEP montre des teneurs sédimentaires de 30.3 à 100 μg.kg^{-1} (62,93 ± 40.97), de 11 à 60.82 μg.kg^{-1} (28.09 ± 16.91), 58 à 216.5 μg.kg^{-1} (117.58 ± 60.30), respectivement. Le 4 n OP a été détecté à 2.08 à 3.72 μg.kg^{-1} seulement aux stations P1, P4 et P11, et le 4-tert-OP n'a pas été détecté. Pour les stations les plus éloignées de l'émissaire, ces composés ont varié de 13,1 à 75 μg.kg^{-1} (33.67 ± 23.73), de 1.68 à 24.24 μg.kg^{-1} (11,11 ± 7,41), de 9.,3 à 55,89 μg.kg^{-1} (23,89 ± 16,78), respectivement. Ces résultats sont très inférieurs à ceux rapportés par Chokwe et al (2015) (NP 93 mg.kg^{-1}) dans les stations d'épuration des boues d'Heraklion, Grèce, Stewart et al (2014) (4NP (<100 - 32000 μg.kg^{-1}) connecté aux usines de traitement des eaux usées de la zone estuarienne d'Auckland, Nouvelle-Zélande, Gong et al (2011b) (NP (31 - 31885 μg.kg^{-1}) des industries fortement urbanisées en Chine et Cespedes et al (2008) (NP (194 mg.kg^{-1}) provenant des boues, reliées aux stations d'épuration de Ter River Catalonia, NE Espagne et Chalaux et al (1992) (NP (370.000 μg.kg^{-1}) provenant des boues d'épuration du bassin de Santa Monica, Californie du Sud. Ces résultats sont du même ordre que ceux observés par Liu et al (2016) (NP (206.6 μg.kg^{-1}) de la zone reliée aux STEP du lac Taihu et de ses tributaires en Chine, Salgiero-Gonzales et al (2015) (NP (74.5 μg.kg^{-1}) pour des activités domestiques, agricoles et nautiques du Bassin fluvial Européen, Portugal, Klosterhause et al (2013) (NP (22 - 86 μg.kg^{-1}) de la zone liée aux STEP de l'estuaire urbain, Grèce.

Statistiquement, comme pour les OCs pesticides et les PCBs, nous avons trouvé qu'il n'y avait pas de corrélation entre les AP et le COT et la la taille des particules. Ces résultats ont montré qu'il y avait d'autres facteurs qui ont contribué à la sorption et la distribution de ces composés.

Là encore, la majorité des stations du côté Est ont des concentrations plus élevées que celles situées à l'ouest. La déviation du panache vers l'est du site est probablement due à la direction du vent dominant, à la turbulence et à la dynamique ascendante présente dans cet écosystème côtier.

De plus, nous avons observé des concentrations en AP significatives relevées dans les échantillons de sols des quatre stations exposées au vent dominant des Calanques de Cortiou. On constate que NP_1, NP_2 et NP_3 varient de 21.32 à 81.87 μg.kg^{-1} (48.08 ± 27.70), 14.42 μg.kg^{-1} à 29,47 μg.kg^{-1} (19.49 ± 6.92), et 142.97 μg.kg^{-1} à 461.12 μg.kg^{-1} (339.13 ± 138.26), respectivement. Alors que le 4-n-OP était trouvé à près de 80.45 μg.kg^{-1} aux stations S1 et S3, le 4 t OP a été détecté à l'état de traces à la station S3. Ces résultats sont largement inférieurs à ceux rapportés par Venkatesan et Halden (2013) qui ont été trouvés près de 534000 μg.kg^{-1} dans les boues et les sols amendés. Marcomini et al (1989) (dans la boue de STEP) et Hawrelak et al (1999) (dans les décharges industrielles) ont également trouvé des teneurs très élevées respectivement de 4750 μg.kg^{-1} et 3640 μg.kg^{-1}. Néanmoins, plusieurs travaux ont trouvé des NPs en plus faibles concentrations comme Andreu et al (2007) ont rapporté 252.83 μg.kg^{-1} dans les décharges de la STEP, tandis que Stanford et Weinberg (2007) ont trouvé seulement 29 μg.kg^{-1} dans la zone d'irrigation. Vikelosoe et al (2002) ont trouvé ces composés dans le *sol naturel de 0,98 à 470 $\mu g.kg^{-1}$. Ces produits chimiques n'ont pas été détectés dans le sol naturel qui a été observé par Gibson et al (2005) au Royaume-Uni.*

Il est clairement montré que la majorité des contaminants des NP ont été trouvés dans les échantillons de sol soumis aux rejets des usines de traitement des eaux usées et aux activités industrielles. Néanmoins, ils ont également trouvé dans le sol naturel ce qui a implique que ces produits chimiques pourraient être disséminés et transportés à partir des différentes matrices dans l'environnement.

D'autre part il a été montré que les stations les plus influencées par le vent de sud-est étaient celles qui présentaient les concentrations plus élevées en APs au niveau des sols de surface. De plus, NP_3 semblait être l'isomère dominant dans toutes les stations. Le point d'émissaire des STEP joue vraisemblablement un rôle important sur la contribution des résidus des APs tant dans les sédiments marins que dans les échantillons de sol. Contrairement aux sédiments, nous avons constaté que ces APs avaient une corrélation significative avec le COT, ce qui explique que la sorption de ces contaminants dans le sol de surface était probablement contrôlée par la matière organique de ces sols.

A notre connaissance, il s'agit de la première étude de ces polluants dans des matrices d'aérosols dans cette zone côtière directement liée au déversoir de la STEP. Les aérosols vecteurs des trois isomères des NPs (NP_1, NP_2 et NP_3) dans l'air ont été mesurés pour cinq tailles différentes, qui sont 0.49 - 0.92 μm, 0.92 - 1.5 μm, 1.5 - 3 μm, 3 - 7.2 μm, > 7.2 μm pour des valeurs en APs variant entre 0,61 et 13,91 $ng.m^{-3}$. De même qu'au niveau des sédiments et des sols, NP_1 et NP_3 sont les isomères prédominants trouvés au niveau des aérosols. Par contre, 4-n-OP et 4-tert-OP n'ont pas été détectés dans les échantillons d'aérosols. Les concentrations les plus élevées de NP_3 ont été mesurées au niveau des particule de 0.92 à 7.2 μm qui sont classées comme aérosols marins primaires (PMA) comme trouvé par Clarke et al (2006) ; Nilsson et al (2001) et Geever et al (2005). Ces particules sont majoritairement derivés du sel marin (Grass et Ayers 1983). D'autre part, nous avons également trouvé une taille de particule avec r <0,25 µm comme une particule en mode fin qui était principalement de sulfate de sel non marin (nss-sulfate).

Ces résultats étaient largement inférieurs à ceux trouvés par Saito et al (2014) chez les Japonais (90 $ng.m^{-3}$) ; Ying et al (2006) aux Etats-Unis (690 $ng.m^{-3}$) dans l'air intérieur, Wilson et al (2001) aux Etats-Unis (100 $ng.m^{-3}$) en zone urbaine. Néanmoins, ces résultats sont supérieurs à ceux rapportés par Moreau-Guigon et Chevreuil (2014) en France (0,9 - 2 $ng.m^{-3}$) en centre urbain ; Berkner et al (2004) en Allemagne (1.7 - 117 $pg.m^{-3}$) en zone montagneuse. De plus, nos résultats sont plus ou moins similaires aux résultats rapportés par Salapasidou et al (2011) en Grèce (4.96 $ng.m^{-3}$) en zone urbaine et industrielle ; Saito et al (2014) chez les Japonais (6 $ng.m^{-3}$) en zone urbaine et Van Ry et al (2000) aux Etats Unis (7 $ng.m^{-3}$) en métropole. Il est important de mentionner qu'il y a eu un enrichissement clair en NP dans les zones influencées par les activités urbaines et industrielles.

Afin de déterminer si ces composés dérivaient des mêmes sources ou non, nous avons quantifié les rapports entre NP/AP. Les indices ont montré des valeurs similaires pour ces différentes matrices (sédiment, sol et aérosol). Les rapports de NP_1 dans les sédiments variaient de 0.13 à 0.53 avec une moyenne de 0,29, tandis que les échantillons de sol étaient observés de 0.07 à 0.16 avec une moyenne de 0.12. Les matrices d'aérosols ont donné 0.10 à 0.36 avec une moyenne de 0.23. Concernant l'isomère NP_2, sa contribution dans les sédiments variait entre 0.09 et 0.16 avec une moyenne de 0.13, alors que les échantillons de sol fournissaient 0.02 à 0.08 avec une moyenne de 0.08 et des aérosols contribués à 0.04 à 0.36 avec une moyenne de 0.15. En ce qui concerne NP_3, les échantillons de *sédiments ont fournissaient 0.37 à 0.73 avec une moyenne de 0.58, tandis que nous avons trouvé les échantillons de sol de 0.45 à 0.88 avec une moyenne de 0.58. Ces ratio diagnostics ont montré que ces matrices ont plusieurs ratios similaires pour les différents isomères étudiés ce qui implique qu'ils pourraient dériver de sources similaires pour une même période d'entrée.*

Finalement, pour évaluer les risques environnementaux associés aux NPs, nous avons comparé nos données avec les basées sur des consensus des lignes de guidage des sédiments et du sol (PNEC, concentration prédite sans effet) (Dong et al 2014, INERIS 2014, Commission européenne 2002). Les résultats ont montré un effet négatif potentiel sur le biote marin (> 39 μ*g.kg*$^{-1}$ *dw) car la majorité des échantillons de sédiments (62.92%) dépassaient la valeur de la PNEC. En ce qui concerne les échantillons de sol, les concentrations d'APs variaient de 3.13 à 396.8* μ*g.kg*$^{-1}$ *poids sec, les concentrations maximales se trouvant aux stations S1, S2 et S3 situées dans le corridor exposé à la direction prédominante du vent. 16% des isomères NP dans les échantillons de sol de cette zone côtière dépassaient les PNEC (300* μ*g.kg*$^{-1}$ *poids sec). Ces résultats ont indiqué qu'il y avait un effet négatif sur les organismes dans les environs les Calanques de Cortiou. Par conséquent, on peut supposer que les sédiments et le sol du Calanques de Cortiou présentaient un risque écologique pour la zone d'étude. Néanmoins, Roberts et al (2006) ont montré pour ces polluants dans les sols qu'il n'y avait pas de risque avéré pour les plantes et les organismes à moins que les teneurs mesurées dépassent 10.000 mg.kg*$^{-1}$ *poids sec. Ces concentrations de NP peuvent être transportées du sol vers les animaux et les plantes environnantes. De plus, il a été montré que l'absorption de NPs par les plantes est très faible. Enfin, lorsque les NPs sont adsorbés sur la phase solide, ils peuvent facilement être lessivés du sol. En tenant compte de tous nos résultats, nous avons conclu que la dissémination des NPs dans le sol ne posait probablement aucun risque environnemental pour les écosystèmes terrestres et la santé humaine.*

Cette étude a indiqué que la plupart des APs se trouvaient dans le sol, ce qui indique que le stock final de ces substances était probablement dans le sol après avoir subi les processus physiques et chimiques dans les autres milieux comme l'eau, les sédiments et l'air.

Finalement, cette surveillance environnementale a permis de déterminer la présence de à des niveaux préoccupants pour 5 grandes classes de micro-polluants organiques (HAP, LAB, OC Pesticides, PCB et Alkylphénols) dans les sédiments. Nous avons également étudié le degré d'imprégnation des sols et étudiés les aérosols collectés au niveau de la Calanque de Cortiou. L'utilisation de valeurs toxicologiques seuil ont permis d'évaluer l'impact environnemental de ces polluants. Les PCBs et les APs sont apparus dans plus de 50% des échantillons analysés à des concentrations excédant les valeurs « sans effet », en particulier pour la communauté benthique marine.

Même si la nouvelle unité de traitement des eaux usées (Géolide) a été mise en œuvre avec un traitement biologique de la dernière génération, ce travail a montré que les effets nocifs liés à ces micro-polluants organiques se sont produits dans les sédiments et également dans les sols. Cependant, considérant d'abord que les sédiments de surface intègrent une période importante, et deuxièmement, la difficulté technique pour obtenir les carottes de sédiments dans cette zone, il était probablement encore trop tôt pour valider les effets positifs du processus biologique de la STEP. Il sera également difficile de prédire quand cette amélioration pourra être mise en évidence. Par conséquent, à l'avenir, il est nécessaire de surveiller régulièrement la contamination des sédiments, des aérosols, du sol et du biote dans les environs de la STEP.

To my parents ***H. Omar Umasangaji*** *and Alm.* ***Zawiah Tulhakimah bt H. Kamaluddin Umasangaji****, my wife* ***Yunita Ramili,*** *my children* ***Denish Mercellino Umasangaji and Alessandro Kevin Umasangaji***

who gave me the world

and, to all those who have pushed me along the way

Acknowledgements

There are so many people that have helped me – personally and scientifically — along this long journey. First, I would like to thank my advisor Prof. Pierre DOUMENQ, you have been an amazing mentor, pushing me, allowing me to grow as a scientist and never wavering in your encouragement and support. I realize that was truly hard for me to attempt working in an environment in which there were a huge number of the differences either cultural aspects or working rhythm. Being an overseas student in the country where I am not a native speaker has created me a strong person not only on the scientific staff but also in terms of socio-cultural side. If it were not for your flexibility and good heart when I was trying to figure out what I wanted to study, my graduate experience would have been very different. I would not be studying what I am today—and what I most enjoy— if it were not for your continued kindness and guidance. You have been a wonderful role model and mentor.

I was lucky to work side by side with Dr. Agung Damar SYAKTI as my co-supervisor during my thesis both in the field and in the laboratory (how hard it was). I appreciate your willingness to explore the world outside of science through your public outreach. Although you may be a scientific workaholic, you have always been tolerant of those who are less so, and I thank you for that. I appreciate the many people and experiences you have introduced me to over the past several years in Marseilles and Aix-en-Provence, the place that have been my second home to be honest. I could not deny that sometimes we had a small debate due to our different opinion or missed understanding of several things.

I especially thank Dr. Yann TERNOIS, who has scientifically mentored me during my thesis writing. You have grown me up with your rigorous personally, high discipline but full of tolerant which was I appreciated a lot.

I have had the fortune during my tenure at LCAE especially the research group of organic micro-pollutants (MPO) to work with many amazing individuals. I owe special thanks Dr. Laurence ASIA who has taught me lots of things in terms of analytical chemistry that I have never learnt before. Though it took me a while to figure out how things worked, I appreciate your knowledge, support, and guidance over the last few years. Stephanie LEBARILLIER who always be ready to help with several lab works such as extraction and purification. The ‘gangster’ those days, Dr. Fehmi KANZARI, Dr. Frederique GANDOLFI, Dr. Delphine KAIFAS, Dr. Benoit CHARASSE Dr. Marie SPIANDORE and Dr. Yudhistira AZIZ, you have filled my days with divers colors. High appreciation for your knowledge and your ability in chemistry I always learned from you, and for that I will always be grateful. Your enthusiasm is contagious and I hope someday to inspire others as you have inspired me. For Dr. Benoit CHARASSE, your scientific insight, words of encouragement, emotional support, and our times together will not be forgotten and have been an integral part of my graduate experience. I still remember the time we passed together on a scientific conference in Dallas – Texas, US.

I am deeply indebted to the *Ecole Doctoral Science de l’Environment*, particularly the directure and directrice of this graduate school Prof. Pierre ROCHETTE and Prof. Kathrine KELLER who had permitted me for several extended registration. Minister of Research and Higher Education of Indonesia for the financial support which has made my education here possible and for their ongoing help and guidance. Ford Foundation and local government who also financially assisted at the time I was about to accomplish these studies.

Of course I also want to thank my parents and siblings. They have always been my number one fans and have provided me with so much support and encouragement over the years. I underwent a very hard period on which I lost my beloved mother and my wife was diagnosed of the cancer (she has been better these days). I admire that those moments have truly influenced my thesis life in France. Fortunately, my two boys who always be my consolation during those difficult time. I promise that I would be able to spend more time with each of you. I am grateful for all that you have given me and love you both from the bottom of my heart.

Also, I offer my thanks to Mr. Max BRESSON and Mr. Jean-Francois BARBION, Mr. Frédéric POITOU, I am grateful for your awesome welcome during my thesis particularly Mr. Max BRESSON for your assistance during our field work at sea. My gratefully acknowledges De Valroger, F and D. Eric for helping with scuba diving and sediment sampling. My new friends who has assisted me immensely during my PhD thesis defense preparation, Nuning Vita HIDAYATI and Clementine COTE.

During my thesis work I have also been awarded a grant from Fulbright to conduct research on fate and occurrence of oil spill at Woods Hole Oceanographic Institution (WHOI) in Massachusetts, US. A great experience I have ever had, working in the different circle and I felt so lucky to recognize two different cultures at the same time during my PhD project (French and American). For this, I owe a huge thanks to Dr. Christopher Reddy and his research group at Marine Chemistry and Geochemistry Lab. I have learnt lots of things related to GC-FID, FTIR and how oil undergoes weathering processes in the environment particularly in the ocean.

Funding for this research was provided by ANR CES grant for MARSECO Project. This work was done in the framework of the research federation ECCOREV. I specially thank the PROTEE team from the University of Toulon. Ministry of Research and Higher Education of Indonesia. I am indebted to these funding sources as well as those writing the grants that supported my education. Thanks for believing in me.

TABLE OF CONTENT

1.4. Linear Alkylbenzenes (LAB)………

1.5. Alkylphenols (APs)

Chapter II. Materials and Methods

Chapter III. Indicator of terrestrial biogenic hydrocarbons contamination and Linear Alkylbenzenes as land-base pollution in marin sediments

Summary
Abstract

Chapter IV. Distribution of organochlorine pesticides (OCs) and polychlorinated bephenyls (PCBs) in marine sediments directly exposed to Wastewater Treatment from Cortiou, Marseilles

Summary
Abstract

Chapter V. Fate and Occurrence of Alkylhenols (APs) in Coastal Area of Cortiou Creek, The Bay of Marseille

Summary
Abstract

5.3. Result and Discussion

LIST OF FIGURES

Chapter I.

Chapter II.

Chapter III.

Chapter IV.

Chapter V.

LIST OF TABLES

Chapter I.

Chapter II.

Chapter III.

Chapter IV.

Chapter V.

LIST OF ABREVIATION

A

ACN	: Acetonitrile
APEOs	: Alkylphenol polyethoxylates
AH	: Aliphatic hydrocarbon
APAH	: Amino polycyclic aromatic hydrocarbon
AFSSA	: Agence française de sécurité sanitaire des aliments
ATSDR	: Agency for Toxic Substances and Disease Registry
ASE	: Accelerated solvent extraction system
AhR	: Aryl hydrocarbon receptor
AR	: Androgen
APERC	: Alkylphenols and Ethoxylates Research Council
ANR	: Agence nationale de la recherche

B

BzA	: Benzo(a)anthracène
Bz(b)Fl	: Benzo(b)fluoranthène
Bz(k)Fl	: Benzo(k)fluoranthène
BaP	: Benzo(a)pyrène
BeP	: Benzo(e)pyrene
BghiP	: Benzo(g,h,i)perylene
BkP	: Benzo(k)pyrène

C

CCME	: Canadian Council of Ministers of the Environment
CAR	: Constitutive anderstane receptor
COHIBA	: Control of hazardous substances Baltic Sea region
CH_2Cl_2	: Dichlorométhane
CH_4	: Méthane
Chry	: Chrysène
CPI	: Carbon preference index
CPL	: Chromatographie d'adsorption préparative

D

DCM	: Dichloromethan
dB(a,h)A	: Dibenzo(a,h)anthracène
DL-PCBs	: Dioxin-like polychlorinated biphenyls
DDT	: Dichlorodiphényltrichloroéthane
DDD	: Dichlorodiphényldichloroéthane
DDE	: Dichlorodiphényldichloroéthylène
DMBA	: 12 - dimethylbenzo anthracene
DSBP	: 4,4' bis (2 – sulfostryryl)biphenol

E

ETBE	: Ethyl tributyl ether
EC	: European council
EU	: European union
EPA	: Environmental Protection Agency
EQS	: Environmental Quality Standards
ER	: Estrogen
ERM	: Effects range median
ERL	: Effects range low
EFSA	: European Food Safety Authority
EDC	: Endocrine-Disrupting Chemicals
EES	: Mission/excitation synchrone
EOM	: Extracted organic matter

F

FAO	: Food and Agriculture Organization
F1	: Hydrocarbures saturés
F2	: Hydrocarbures aromatique
F3	: Polar compounds
Fl	: Fluoranthène
FS	: Full scan

G

GC-FID	: Gas chromatography – flame ionization detector
GC-MS	: Gas chromatography - mass spectrometry
GJIC	: Gap junctional intercellular communication

H

HCPI	: High carbon preference index
HCT	: Hydrocarbures saturés + hydrocarbures aromatiques
HMW	: High molecular weight
HPLC	: High performance liquid chromatography
HCH	: Hexachlorocyclohexane
HRGC-FID-ECD	: High-resolution gas chromatography - flame ionization detection - Electron-Capture Detection.
HRGC-MSD	: High-resolution gas chromatography mass selective detector

I

IUPAC	: International Union of Pure and Applied Chemistry
IARC	: International Agency for Research on Cancer
ICES	: International Council for the Exploration of the Sea
ISQG	: Interim Sediment Quality Guidelines
I/E	: Internal/External
IPCS	: International Programme on Chemical Safety
IAEA	: International atomic energy agence
IARC	: International agency for research on cancer
IOC	: Intergovernmental oceanographic commission
IndP	: Indéno (1,2,3,c-d) pyrène
INERIS	: Institut national de l'environnement industriel et des risques

L

LAB	: Linear alkylbenzenes
LAS	: Linear alkylbenzenes sulfonat
LRAT	: Long-range atmospheric transport
LCPI	: Low carbon preference index
LMW	: Low molecular weight
LOUS	: List of undesirable substances
LOD	: Limit of detection
LOQ	: Limit of quantification
LOEC	: Lowest observed effect concentration

M

MeOH	: Méthanol
MOPI	: Marine oil pollution index
MPE	: Multicellular photosynthetic eucaryote
MTBE	: Methyl tert buthyl ether
MAE	: Microwave assisted extraction

N

NPAH	: Nitrated polycyclic aromatic hydrocarbons
NDL-PCBs	: Non-dioxinelike polychlorinated biphenyls
NPs	: Nonylphenols
NPEO	: Nonylphenol ethoxylates
NAR	: Natural n-alkane ratio
NOEL	: No observed effects concentration

O

OPEO	: Octylphenol polyethoxylates
OSPAR	: Oslo Paris (Convention)
OCs	: Organochlorines
OHPAH	: Hydroxylated polycyclic aromatic hydrocarbons
O	: Oxygène

P

PAHs	: Polycyclic aromatic hydrocarbons
PCBs	: Polychlorinated biphenyls
PXR	: Pregnant X receptor
PEL	: Probable effect level
PNEC	: Predicted no-effect contamination
PCA	: Principale component analysis
Phy	: Phytane
Ph	: Phénanthrène
Pr	: Pristane
PSS	: Programmed split/splitless
Py	: Pyrène

R

REE : Rare earth elements
RFG : Reformulated gasoline
ROS : Reactive oxygen species

S

SQGs : Sediment Quality Guidelines
SEEF : Social Economic and Environmental Factors
STP : Standard temperature and pressure
SIM : Selected ion monitoring
S : Sulphure
Sq : Squalane
Squa : Squalène

T

TSCA : Toxic Substances Control Act
TAR : Terrigenous / aquatic ratio
TEC : Treshold effect level
TC : Total carbon
TOC : Total organic carbon

U

UCM : Unresolved complex mixture
UNEP : United nations environment programme
US-EPA : United states-environmental protection agency
UV : Ultra-violet
UNECE : United Nations Economic Commission for Europe
UN : United Nations

W

WWTPs : Wastewater treatment plants

Introduction

The population growth of our planet over the last century is unprecedented. In a hundred years, its population has increased, from 1.7 billion to 7.6 billion, which is drastically affecting the production and consumption patterns of chemicals and industry products (Ngô and Régent, 2012). This issue has had a strong impact on our planet, particularly the marine environment (Ahmed *et al* 2017; Ke *et al* 2017; Monaco *et al* 2017; Sarker *et al* 2018) and human health (Tongo *et al* 2017; Wang *et al* 2017; Kadi *et al* 2018). These chemicals and industrial products encompass organic micro-pollutants (Iwata *et al* 1994; Pereira *et al* 1994; Banjoo and Nelson 2005; de Mora *et al* 2005; Fung *et al* 2005; Numata *et al* 2005; Duodu *et al* 2017; Polidoro *et al* 2017) and inorganic ones (Tranchida *et al* 2010; Marchand *et al* 2012; Yoo *et al* 2013; Harikrishnan *et al* 2017; Ashraf *et al* 2018; Naifar *et al* 2018).

These organic compounds, which are widespread in the environment, are potentially impactful. Not only because of their emission modes, but also their persistence and accumulation in the environment. Among these organic micro-pollutants, encompassing polycyclic aromatic hydrocrbon (PAHs), linear alkylbenzene (LAB), organochlorine pesticide (OCs), polychlorinated biphenyls (PCBs), and the emerging pollutants emitted by wastewater treatment plants (WWTPs) such as alkylphenols as a raw material in detergent manufacture. They are interesting and attracting the attention of scientific society due to their environmental problems. The majority of these products today are employed in various sectors, from domestic to industrial uses, which can induce their accumulation not only into the environment, (Harman *et al* 2009 ; Duan *et al* 2014; Staniszewska *et al* 2015; Couderc *et al* 2016; Jeon *et al* 2017) but also their bioaccumulation potential to the marine organisms as one of the natural resources essential for human beings (Cailleaud *et al* 2007; Couderc *et al* 2015; Ademollo *et al* 2017; Staniszewska *et al* 2017).

The occurrence of PAHs in the marine environment comes from two principal sources : petrogenic source which is derived from hydrocarbons which are associated with spills of crude and refined oil (Duan *et al* 2018; Han *et al* 2018; Pongpiachan *et al* 2018; Perez-Umphrey *et al* 2018) and a pyrogenic source which includes compounds derived from fossil fuel combustion, waste incineration, biomass burning and asphalt production (Keshavarzifard *et al* 2017; Pokhrel *et al* 2017; Yang *et al* 2017; Škrbić *et al* 2018). At the same time, linear alkylbenzenes (LABs) are the chemical markers derived from commercial detergents through wastewater treatment effluents. These come directly from domestic, industrial activities and atmospheric input (Eganhouse *et al* 1988; Wang *et al* 2012; Zhang *et al* 2012; Wei *et al* 2014; Venturini *et al* 2015) Subsequently, PCBs which are considered as classical persistent organic pollutants (POPs) releasing into the marine environment from industries and domestic usages such as heat exchange fluids in electric transformers and capacitors, as an additive in paints, carbonless copy paper and plastics, frequently discovered in various environmental matrices (Pan *et al* 2007; Okay *et al* 2009; Kampire *et al* 2015; Alegria *et al* 2016; Oziolor *et al* 2018). Meanwhile, pesticides are particularly fluxed to the marine environment from agricultural areas; since they are used as agricultural pest controls, from urban discharges and other industries. Over the last six decades, pesticides have been extensively used as a thermal stabilizer in the plastic industry and as biocides in shipyards and marine buildings. Despite being banned, these chemicals are frequently found in the marine environment (Alonso-Hernández *et al* 2015; El Nemr and El-Sadaawy 2016; Buah-Kwofie and Humphries 2017; Qu *et al* 2017; Dang *et al* 2018).

We have investigated one of the organic micro-pollutants families which are categorized as nonionic surfactant alkylphenols (APs.) These chemicals are used as raw materials to produce APEOs in the manufacture of detergents and the preparation of phenolic resins, polymers, heat stabilizer, antioxidants, and curing agents (Duan *et al* 2014). They mainly enter into the marine environment through biodegradation processes of APEOs via treated and untreated discharged water, and also livestock activities (Renner 1997; Chen *et al* 2005; Liu *et al* 2016; Jeon *et al* 2017; Staniszwska *et al* 2017).

Several of these chemicals are mutagenic and carcinogenic (Li *et al* 2014; Yang *et al* 2015; Ali *et al* 2017; Cetin *et al* 2018; Malarut and Vangnai 2018). Some of these disrupt the endocrine system in humans and other animals (Annamalai and Namasivayam 2015; Grześkowiak *et al* 2016; Priac *et al* 201; Balaguer and Bourguet 2018; He *et al* 2018; Ramalho-Santos and Tavares 2018; Vilela *et al* 2018). However, to date, they are still being discovered in food, human blood and urine (Ferrara *et al* 2011; Mezcua *et al* 2012; Sun *et al* 2012; Azzouz *et al* 2016; Shekhar *et al* 2017; Chung *et al* 2018; Ferrante *et al* 2018). Due to their bioaccumulation and toxicity towards the environment, organisms and human beings (Çok *et al* 2012; García-Alvarez *et al* 2014; Luzardo *et al* 2014; Giuliani *et al* 2015; Saija *et al* 2016; Besis *et al* 2017; Kilunga *et al* 2017; Wang *et al* 2017), the application of these substances has been banned in many countries of the world through the regulation and legislation established by local ministerial councils.

Several investigations have revealed that the emission of these pollutants have exceeded environmental toxic effects to the marine environment. This indicates the adverse effects of living organisms in the surrounding ecosystem. The contaminants are encountered into the littoral area, encompassing PAH (Li *et al* 2016; Hong *et al* 2016; Rajpara *et al* 2017; Zeng *et al* 2018), LABs (Medeiros and Bicego 2004; Montone *et al* 2010; Dwiyitno *et al* 2016; Masood *et al* 2016) OCs Pesticides, PCBs (Barakat *et al* 2013 ; da Silva *et al* 2016 ; Nemr and El-Sadaawy 2016 ; Rizzi *et al* 2017) and Alkylphenols (Beyer *et al* 2012; Bizarro *et al* 2014; Salgueiro-González *et al* 2015; Dong *et al* 2015). This suggests that these substances are still applied to both domestic and industrial scales. Additionally, WWTPs cannot completely eliminate new contaminants such as detergents and some emerging pollutants (Golovko *et al* 2014; Zhang *et al* 2015; Coba *et al* 2018).

The decision on persistent organic micro-pollutant usage should be taken into account that their risks of emissions versus alternative compounds are based on a thorough understanding of their behavior in the marine environment. On the understanding of how concentration levels in the different environmental matrices, the prediction of environmental risk and how they are particularly responsive to the coastal dynamics are the essential matters to an environmental management marine ecosystem in the future. Our investigation shows how these chemicals have been affected by the plume dynamic in front of WWTPs's emissary point. The impacts of these pollutants in the environment are crucial for determining appropriate responses to their emissions, abating damages and assisting in clean up and restoration.

The Bay of Marseilles, which has about one million inhabitants, suffered a strong urban impact, industrial, port activities and tourism. On the other hand, the creation of Calanques National Park in 2012, which is located just outside of Marseilles, is the first suburban National Park in both terrestrial and marine ecosystems (about 8300 hectare (land) and 43.500 hectare (marine). In the summer season, there are more than 1,400 boats anchored in the creeks. Beside, this site has the particularity to host the envoy rejects of WWTPs in Cortiou after treatment and also has 16 other cities (Asia 2012, *thesis unpublished*).

Concerning multiple conditions and various effects in this area, we are viewing that the comprehensive work on several organic micro-pollutants is truly interesting. These exclude concentration levels, sources of origins and spatial distribution through the plume of an emissary point under the influences of several factors.

We have chosen this study site because it is an extremely populated area, (approximately 1,000,000) which has an impact of urbanized industrial activities in the maritime port of Marseilles. Additionally, the touristic activities in several areas such as Sausset-les-Pins, Carry-le-Rouet, l'Estaque, Vieux Port and port de La Pointe Rouge contribute to the environmental risk in terms of emerging pollutants. This condition has been quite complicated since the National Park of Calanque was established in 2012. Since the various activities have taken place in this bay, we are considering that the intense research on the contamination levels of these organic micro-pollutants will be the interesting research in the future.

There have been numerous previous works on the distribution of these chemicals in this study site. Nevertheless, studies on linear alkylbenzenes (LABs) and alkylphenols (APs) in the sediments along with the dynamic of the plume at the WWTP's outfall under the influences of the wind and hydrodynamic factors is the very first investigation.

This thesis work fits into this context in order to have a better knowledge and understanding of the contamination of marine surface sediments directly connected to WWTPs, particularly Cortiou Creek, in the Bay of Marseilles. This area has special characteristics due to their geographical location (Mediterranean typically) and also the number of anthropic activities (urban, industrial and agricultural) in their watersheds.

The first chapter is devoted to the general description of nature, physicochemical properties, various sources of their existence in the environment and the environmental risks of all these organic pollutants to the marine ecosystem and human health. We have also reviewed the alteration of those compounds once they intered into the environment, accompanied with microbial organisms that play an essential role for this matter, the different analytical methods which have been developed during the last three decades in order to obtain the validities and the robustness of the results. Also, we would like to recognize how the methods have been re-evaluated during this time. The synthesis of concentration estimations in marine sediments throughout the world according to the articles published on the International Journals has been studied as well.

The second chapter begins by introducing the sampling site in Cortiou Creek, the Bay of Marseilles and the strategy sampling campaign, this will be followed by the analytical methods to identify and quantify these compounds in order to meet the objectives.

In the third chapter, we are going to discuss about the characterization and the existence of petroleum hydrocarbon pollution in Cortiou sediments, particularly n-alkane and polyaromatic hydrocarbons (PAHs) pollution, ‘‘sewage tracer’’ compounds, such as LABs, as by-products of LAS detergents, which are the most widely used anionic surfactants. Additionally, we are going to attempt to establish whether the municipal water discharge is responsible for the presence of these pollutants by determining the concentrations and distributions of individual n-alkanes, 16 EPA priority PAHs and LABs in surface sediments of the Cortiou Creek in relation to the carbon content and organic carbon in the sediment.

The fourth chapter highlights the distribution of OCs and PCBs in the sediments and their potential recent contamination through indices of pollution and potential environmental risk as well as their temporal trends after the 1970–1980 ban in comparison with other studies in the area.

The fifth chapter tackles the extent of Alkylphenols (APs) in three different compartments (sediments, soil and the most explorative one namely aerosol). In addition, we are going to attempt to describe the fate and occurrence of these compounds and their toxicity potential to the marine benthic ecosystem through predicted non-effect concentration (PNEC). This estimation also provides a new insight of their potential impact to human health in the surrounding littoral area of Marseilles Bay.

CHAPTER 1. BIBLIOGRAPHY

1.1. Hydrocarbons

Presentation

Hydrocarbons, as their name indicates, are compounds of carbon and hydrogen. As such, they represent one of the most significant classes of organic compounds on earth. In methane (CH_4 the simplest saturated alkane, a single-carbon atom, is bonded to four hydrogen atoms. In the higher homologs of methane (of the general formula C_nH_{2n+2}) all atoms are bound to each other by single (sigma (σ) two-electron two-center) bond with carbon displaying its tendency to form C--C bonds. Whereas, in CH_4, the H : C ratio is 4, in C_2H_6 (ethane), it decreased to 3 : in C_3H_8 (propane), to 2.67 ; and so on. Alkane can be straight chain (with each carbon attached to not more than two other carbon atoms) or branched (in which at least one of the carbons is attached to either three or four other carbon atoms). Carbon atoms can be aligned in open chains (acyclic hydrocarbons) or can form rings (cyclic hydrocarbons) (Olah and Molnar 2003).

Subsequently, cycloalkanes are cyclic saturated hydrocarbons containing a single ring. Bridged cycloalkanes contain one (or more) pair(s) of carbon atoms common to two (or more) rings. In bicycloalkanes there are two carbon atoms common to both rings. In tricycloalkanes there are four carbon atoms common to three rings such as in adamantane (tricycle (3.3.1) decane), giving a caged hydrocarbon structure. Carbon can also form multiple bonds with other carbon atoms. This results in unsaturated hydrocarbons such as olefins (alkenes, C_nH_{2n}), specifically, hydrocarbons containing a carbon–carbon double bond or acetylenes (alkynes, C_nH_{n-2}) containing a carbon–carbon triple bond. Whereas, dienes and polyenes contain two or more unsaturated bonds.

Moreover, **aromatic hydrocarbons (arenes)**, a class of hydrocarbon of which benzene is parent, consist of cyclic arrangement of formally unsaturated carbons, which, however, give a stabilized (in contrast to their hypothetical cyclopolyenes) delocalized *p* system. The H : C ratio in hydrocarbons is indicative of the hydrogen deficiency of the system. As mentioned, the highest theoretical H : C ratio possible for hydrocarbons is 4 (in CH_4), although in carbocationic compounds (the positive ions of carbon compound) such as CH_5^+ and even CH_6^{2+} the ratio is further increased (to 5 and 6, respectively). On the other hand, the scale in extreme cases, such as the dihydro or methylene derivatives of recently discovered C_{60} and C_{70} fullerenes, the H : C ratio can be as low as ~0.03.

Nomenclature

The International Union of Pure and Applied Chemistry (IUPAC) established rules to name hydrocarbons. Frequently, however, trivial names are also used and will continue to be used. Systematic naming is mostly followed. Trivial (common) naming, however, also well extended. *Olefins or aromatics* clearly are very much part of our everyday usage, although their IUPAC names are *alkenes* and *arenes*, respectively. Straight-chain saturated hydrocarbons are frequently referred to as n-alkanes (normal) in contrast to their branched analogs (isoalkanes, *i*-alkanes). Similarly straight-chain alkenes are frequently called n-alkenes as contrasted with branch isoalkenes (or olefins). What needs to be pointed out, however, is that one should not mix the systematic IUPAC and the still prevalent trivial (or common) namings. For example, $(CH_3)_2C{=}CH_2$ can be called isobutylene or 2-methylpropene. It, however, should not be called isobutene as only the common name butylene should be affixed by iso. Moreover, isobutane is the proper common name for 2-methylpropane $[(CH_3)_3CH]$.

Concerning this work, we are interested in aliphatic hydrocarbon (AH) particularly saturated ones since these compounds occurred in various environmental matrices such as in soil (Serrano *et al* 2008; Rushdi *et al* 2013; Zhang *et al* 2018), sediment (Lima *et al* 2012; Vaezzadeh *et al* 2015; Assuncao *et al* 2017; Pu *et al* 2017), water (Bhattacharyya *et al* 2015; Akhbarizadeh *et al* 2016), biota (Amodio-Cocchieri *et al* 2003; Crespo *et al* 2004; Tolosa *et al* 2005; de Mora *et al* 2010; Harvey *et al* 2014; 2017) and also food (Zhang *et al* 2018; Adams *et al* 2011). Additionally, the most environmental and human health risk is polycyclic aromatic hydrocarbons (PAHs). Some individuals of these compounds found in the environmental matrices suggested to be carcinogenic potential as revealed recently by some authors throughout the globe (Sarigiannis *et al* 2015; Abdur Rehman *et al* 2017; Ali *et al* 2017; Franco *et al* 2017; Sun *et al* 2017; Benson *et al* 2018; Galvão *et al* 2018; Gope *et al* 2018; Hamid *et al* 2018; Pokhrel *et al* 2018; Singh and Agarwal 2018; Tarafdar and Sinha 2018).

Since their environmental and human risks, European Union established some legislative references concerning these chemicals namely Commission Regulation EU No 835 - 836/2011 to the foods. Commission Recommendation (2005/108/EC) of 4 February 2005 on the further investigation into the levels of PAHs in certain foods particularly several compounds in 16 PAHs.

1.1.1. Aliphatic hydrocarbons

An aliphatic hydrocarbon compound is a hydrocarbon compound containing carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings (Figure 1.1). Aliphatic compounds are probably saturated (e.g., hexane and other alkanes) or unsaturated (e.g., hexane and other alkene, as well as alkynes). The simplest aliphatic hydrocarbon is methane, CH_4. In addition to hydrogen, other elements may be bonded to the carbon atoms in the chain, including oxygen, nitrogen, chlorine and sulfur. Most Aliphatic Hydrocarbons are flammable (e.g., ethylene, isooctane, acetylene).

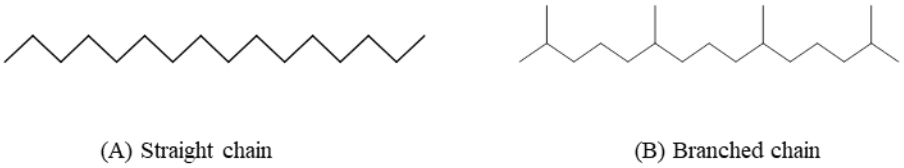


Figure 1.1. The examples of aliphatic hydrocarbons

1.1.1.1. Physical Properties of AH

Alkanes and cycloalkanes are nonpolar substances. Attractive forces between alkane molecules are dictated by London forces (or dispersion forces, arising from electron fluctuations in molecules and are weak. Thus, alkanes have relatively low boiling points compared with polar molecules of comparable molecular weight. The boiling points of alkanes increase with increasing number of carbons. This is because the intermolecular attractive forces, although individually weak, become cumulatively more significant as the number of atoms and electrons in the molecule increases.

Furthermore, for a given number of carbon atoms, an unbranched alkane has a higher boiling point than any of its branched-chain isomers. This effect is evident upon comparing the boiling points of selected C_8H_{18} isomers. An unbranched alkane has a more extended shape, thereby increasing the number of intermolecular attractive forces that must be broken in order to go from the liquid state to the gaseous state. On the other hand, the relatively compact ellipsoidal shape of 2,2,3,3-tetramethylbutane permits it to pack into a crystal lattice more effectively than octane and so raises its melting point.

In general, solid alkanes do not often have high melting points. Unbranched alkanes tend toward a maximum in that the melting point of $CH_3(CH_2)_{98}CH_3$ (115 °C [239 °F]) is not much different from that of $CH_3(CH_2)_{148}CH_3$ (123 °C [253 °F]). The viscosity of liquid alkanes increases with the number of carbons. Increased intermolecular attractive forces, as well as an increase in the extent to which nearby molecules become entangled when they have an extended shape, cause unbranched alkanes to be more viscous than their branched-chain isomers. The densities of liquid hydrocarbons are all less than that of water, which is quite polar and possesses strong intermolecular attractive forces. All hydrocarbons are insoluble in water and, being less dense than water, float on its surface. Hydrocarbons are, however, usually soluble in one another as well as in organic solvents such as diethyl ether ($CH_3CH_2OCH_2CH_3$).

1.1.1.2. Chemical properties of AH

Concerning this work, we propose an example of a saturated AH namely, alkane, this compound is not very reactive when compared with other chemical species. This is because the backbone carbon atoms in alkanes have attained their octet of electrons through forming four covalent bonds (the maximum allowed number of bonds under the octet rule; which is why carbon's valence number is 4). These four bonds formed by carbon in alkanes are sigma bonds, which are more stable than other types of bond because of the greater overlap of carbon's atomic orbitals with neighboring atoms' atomic orbitals. To make alkanes react, the input of additional energy is needed; either through heat or radiation.

Gasoline is a mixture of the alkanes and unlike many chemicals, can be stored for long periods and transported without problem. It is only when ignited that it has enough energy to continue reacting. This property makes it difficult for alkanes to be converted into other types of organic molecules. Alkanes are also less dense than water, as one can observe, oil, an alkane, floats on water.

Alkanes are non-polar solvents. Since only C and H atoms are present, alkanes are nonpolar. Alkanes are immiscible in water but freely miscible in other non-polar solvents. Alkanes consisting of weak dipole dipole bonds can not break the strong hydrogen bond between water molecules hence it is not miscible in water. The same character is also shown by alkenes. Because alkanes contain only carbon and hydrogen, combustion produces compounds that contain only carbon, hydrogen, and/or oxygen. Like other hydrocarbons, combustion under most circumstances produces mainly carbon dioxide and water. However, alkanes require more heat to combust and do not release as much heat when they combust as other classes of hydrocarbons. Therefore, combustion of alkanes produces higher concentrations of organic compounds containing oxygen, such as aldehydes and ketones, when combusting at the same temperature as other hydrocarbons.

Alkanes are also known as paraffins, or collectively as the paraffin series. These terms are also used for alkanes whose carbon atoms form a single, unbranched chain. Branched-chain alkanes are called isoparaffins.

Methane through Butane are very flammable gases at standard temperature and pressure (STP). Pentane is an extremely flammable liquid boiling at 36°C and boiling points and melting points steadily increase from there ; octadecane is the first alkane which is solid at room temperature. Longer alkanes are waxy solids ; candle wax generally has between C_{20} and C_{25} chains. As chain length increases ultimately we reach polyethylene, which consists of carbon chains of indefinite length, which is generally a hard white solid.

1.1.1.3. Sources and occurrence of AH

The most abundant sources of alkanes are natural gas and petroleum deposits, formed over a period of millions of years by the decay of organic matter in the absence of oxygen. Natural gas contains 60–80 percent methane, 5–9 percent ethane, 3–18 percent propane, and 2–14 percent higher hydrocarbons. Petroleum is a complex liquid mixture of hundreds of substances—including 150 or more hydrocarbons, approximately half of which are saturated.

Moreover, approximately two billion tons of methane is produced annually by the bacteria that live in termites and in the digestive systems of plant-eating animals. Smaller quantities of alkanes also can be found in a variety of natural materials. The so-called aggregation pheromone whereby Blaberus craniifer cockroaches attract others of the same species is a 1:1 mixture of the volatile but relatively high-boiling liquid alkanes undecane, $CH_3(CH_2)_9CH_3$, and tetradecane, $CH_3(CH_2)_{12}CH_3$. Hentriacontane, $CH_3(CH_2)_{29}CH_3$, is a solid alkane present to the extent of 8–9 percent in beeswax, where its stability and impermeability to water contribute to the role it plays as a structural component. With the exception of the alkanes that are readily available from petroleum, alkanes are synthesized in the laboratory and in industry by the hydrogenation of alkenes. Only a few methods are available in which a carbon-carbon bond-forming operation gives an alkane directly, and these tend to be suitable only for syntheses carried out on a small scale.

To date, research and exploration of petroleum and natural gas are still being carried out in the various places in the world due to their economic interests. Based on organic geochemical analysis, as that conducted in Yemen (Al-Areeq *et al* 2018). Through organic matter characterization and thermal history of two potential source rock's in Zagros basin, Southwest Iran (Elyasi 2016). Additionally, geological work by Rare Earth Element (REE) geochemistry analysis to determine the petroleum source rocks from northwestern Niger Delta in Africa (Akinlua *et al* 2016). Murillo *et al* (2016) characterized oils and condensates hosted in Triassic and Jurassic reservoirs, established genetic relationships and to assess maturity, mixing and petroleum alteration processes in Sothwestern of Barent Sea.

Furthermore, natural gas, as one of AH sources is currently assessed in a few areas in the world from Asia to Europe and from America to Middle East. In Norway continental shelf is being explored of natural gas (Söderbergh *et al* 2016; Berntsen *et al* 2018), in China (Lu *et al* 2015; Guan *et al* 2017), in Latin America (Chávez-Rodríguez *et al* 2016) in North America (Soeder 2018) in Middle East and North Africa (Khatib 2014) in Turkey (Berk and Ediger 2018) and in Iran (Hafeznia *et al* 2017).

Since most part of our earth is being investigated to exploit the hydrocarbons to human needs, it is logically that these compounds are being emitted into the environment. If there is not an intensively assessment to provide a complete information as a guide line of the environmental policy, the adverse effects will appear in several places in the future.

1.1.1.4. Use

Refined Petroleum Products

As discussed above, hydrocarbons (oil and gas) are used primarily as fuels to generate energy and for space heating. Refined petroleum products provide gasoline, diesel fuel, heating oil, lubricating oil, waxes, and asphalt. A relatively small (4%) portion of oil is used as raw material to produce chemical products essential to our everyday life ranging from plastics to textiles to pharmaceuticals, and so on.

Transportation Fuels

A specific role is assigned to fuels to propel cars, trucks, airplanes, and other vehicles. They are generally referred to as transportation fuels. The impact of the internal-combustion engine on our lives is fundamental. It allowed mankind to achieve mobility via easy means of transportation of persons and goods alike. In less than a century this revolution has transformed and eased our lives but at the same time raised new challenges. Gasoline and diesel fuels are used worldwide in enormous amounts and are produced by the petroleum industry by oil refining. Liquid transportation fuels are conveniently transported, distributed, and dispensed directly into our vehicles and aircraft. Increased environmental concerns did much to begin to assure cleaner burning of our fuels. In the United States, law requires significant reduction of emissions and resulted in lead-free and more recently reformulated gasoline (RFG) containing oxygenates for cleaner burning. At the same time they did not fundamentally change the existing technology. To find alternate fuels to supplement our oil reserves and to ensure cleaner fuels, much further effort is needed.

As long as the internal-combustion engine will remain as the mainstay of our transportation technology, liquid fuels by their convenience and ease of distribution through the existing system will be preferred. Liquefied natural gas (LNG) or methane certainly are clean-burning, high-energy-content fuels, but their widespread use in transportation systems is limited by the difficulty of handling highly volatile and inflammable gases, necessitating the use of heavy pressure vessels to be used as fuel tanks (with associated safety hazards).

Commercial gasoline must provide sufficiently high octane numbers for present day engines. Organometallic additives, such as tetraethyl lead used to achieve higher octane numbers, interfere with catalytic converters (which assure cleaner exhausts) and were (or are) phased out. To maintain needed octane numbers, oxygenated additives, such as alcohols or ethers [e.g., tert-butyl methyl ether or tert-butyl ethyl ether (MTBE and ETBE)] are added to gasoline]. These oxygenates are produced on large scale by the petrochemical industry. In the United States about 85% of RFG contained MTBE and 8% contained ethanol in 1999/97. More recently, however, there has been growing concern about the use of MTBE following its detection in water supplies in California, Maine, and other states. 98 MTBE is soluble in water, moves rapidly in groundwater, and has an unpleasant taste and odor.

In addition, it is difficult to remove from water and persistent to microbial degradation. Although its health effects are not exactly known, legislatures are under pressure to scale back or eliminate MTBE use. The main sources of MTBE contamination are leaks from underground tanks and pipeline spills and leaks. Naturally, MTBE is only part of the contamination problem; banning MTBE would remove only MTBE without addressing the problem of the hydrocarbon contamination. The ban of MTBE and, at the same time, maintaining air quality require the increase of the use of other oxygenates. Ethanol could be the best candidate as the main blending component. Isomerization of straight-chain to branched alkanes also increases the octane number, as do alkylates produced by alkene–isoalkane alkylation (such as that of isobutane and propylene, isobutylene, etc.). These large-scale processes are by now an integral part of the petroleum industry. Refining and processing of transportation fuels became probably the largest-scale industrial operation.

A much pursued alternative to the internal-combustion engine in transportation vehicles is electric propulsion. Electric vehicles thus far have been used for only specific and limited applications, although they are clean, noiseless, and safe. The main difficulty is that existing batteries are relatively inefficient to provide suitable range at reasonable weights. Pending a major breakthrough in battery technology, this will greatly hinder the wider use of electric vehicles. It also must be kept in mind when considering clean electricity-powered vehicles that we are only transferring the potential environmental pollution from individual vehicles to the electric power plants where electricity is generated by combustion of fossil fuels (if not nuclear). In large power plants, however, pollution can be controlled more efficiently.

Chemicals and Plastics

About 4% of petroleum is used as raw material for the chemical and plastics industries. It was coal tar-based aromatics and calcium carbide-based acetylene that led to the establishment of the chemical and plastic industries. World War II, however, brought about rapid development of the petrochemical industry with ethylene becoming the key starting material. A large variety of the chemical and plastics products are now produced.

Since people still explore and use these hydrocarbons, the environmental impacts still exist in the various matrices. Thus, research on the occurrence of these chemical is necessary to be carried out to provide the intensive information for better understanding and new insights of control strategies both in local scale and global one.

1.1.2. Polycylic Aromatic Hydrocarbon

Presentation

The term ‘‘PAH” refers to compounds consisting of only carbon and hydrogen atoms as we mentioned earlier. Chemically, the PAHs are comprised of two or more benzene rings bonded in linear, cluster, or angular arrangements (Di-Toro *et al* 2000; Arey *et al* 2003; Abdel-Shafy and Mansour 2016). Such molecular arrangements are illustrated in (Fig. 1.2). Although there are many PAHs, most regulations, analyses, and data reporting focus on only a limited number of PAHs, typically between 14 and 20 individual PAH compounds. Polycyclic aromatic hydrocarbons have two or more single or fused aromatic rings with a pair of carbon atoms shared between rings in their molecules. PAHs containing up to six fused aromatic rings are often known as ‘‘small” PAHs, and those containing more than six aromatic rings are called ‘‘large” PAHs. The majority of research on PAHs has been conducted on small PAHs due to the availability of samples of various small PAHs. The simplest PAHs, as defined by the International Agency for Research on Cancer (IARC 2010), are phenanthrene and anthracene, which both contain three fused aromatic rings. On the other hand, smaller molecules, such as benzene, are not PAHs. Naphthalene, which consists of two coplanar six-membered rings sharing an edge, is another aromatic hydrocarbon. Therefore, it is not a true PAH, though is referred to as a bicyclic aromatic hydrocarbon. The most extensively studied PAHs are 7, 12-dimethylbenzo anthracene (DMBA) and benzo(a)pyrene (BaP) (CCME 2010). The most commonly analyzed PAHs are given in (Fig. 1.3).

Moreover, these chemicals are a class of several hundred individual compounds defined to be composed of two or more fused aromatic rings. PAHs are of concern because certain of them are classified as probable human carcinogens (IARC 1983; IPCS 1998; UNECE 1998; Vestreng and Klein 2002) and show tumorigenic activity and endocrine disrupting activity in mammals (Cavalieri and Rogan, 1998). Unsubstituted PAHs are formed mainly by the incomplete combustion of organic materials (Baek *et al* 1991; Mastral *et al* 2000). And the atmospheric photochemical PAH reactions cause to form many kinds of substituted PAHs, such as nitrated PAHs (NPAHs), hydroxylated PAHs (OH-PAHs), amino-PAHs (APAHs) and so on. For example, NPAHs are formed easily (Lin-Bin *et al* 2007).

Recently, it has been several times of EU Legislation amending on PAH in food due to the environmental and human risk particularly carcinogenic ones. These are the most recent regulations : Regulation (EU) 2015/1125 amending regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in Katsuobushi (dried bonito) and certain smoked Baltic herring. Regulation (EU) 2015/1933 amending regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in cocoa fibre, banana chips, food supplements, dried herbs and dried spices.

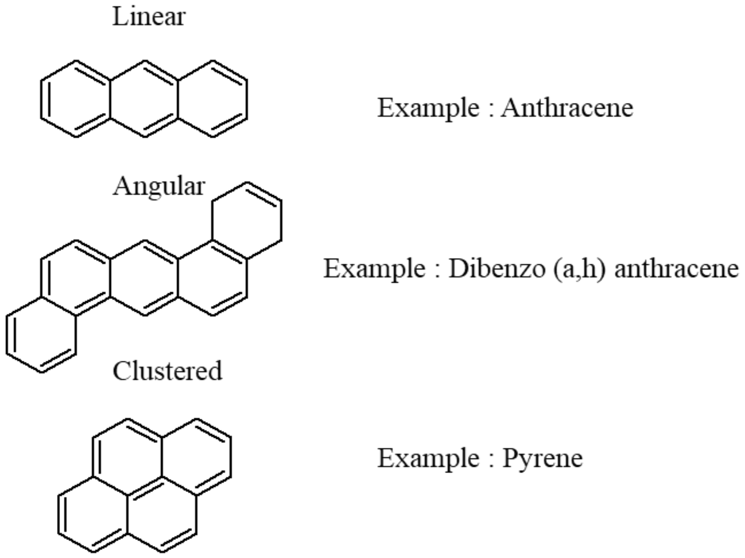


Figure 1.2. Molecular arrangements of PAHs

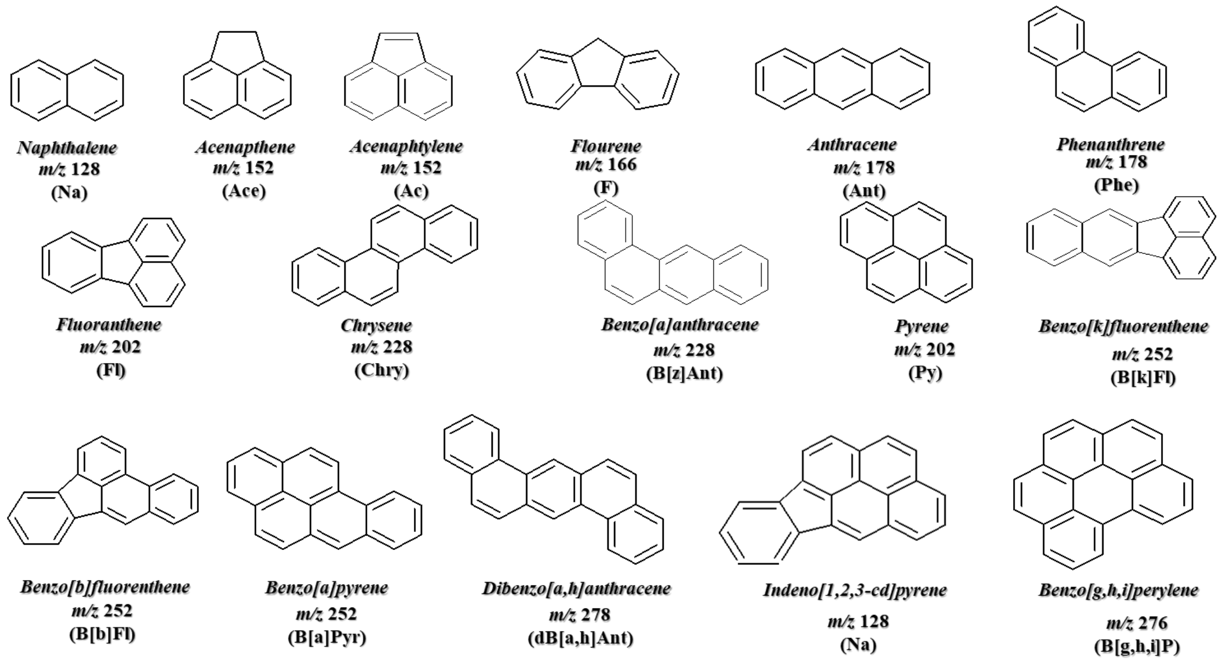


Figure 1.3. Structural formulae of the 16 polycyclic aromatic hydrocarbons defined as priority substances by the United States Environmental Protection Agency (US-EPA)

1.1.2.1. Physical and chemical properties

Generally, the characteristics of these chemicals are high melting and boiling points ; hence they are solid, low vapor pressure and very low aqueous solubility (Masih *et al* 2012). The latter two properties tend to decrease with augmenting molecular weight; conversely, resistance oxidation and reduction raise (Masih *et al* 2012).

Aqueous solubility of PAHs decreases for each additional ring (Masih *et al* 2010). Meanwhile, PAHs are very soluble in organic solvents because they are highly lipophilic. PAHs also manifest various functions such as light sensitivity, heat resistance, conductivity; emit ability, corrosion resistance, and physiological action (Akyüz and Cabuk, 2010).

Additionally, all PAHs are either liquids or solids at room temperature, none are gases. They are insoluble in water. Benzene was once widely used as a solvent, but evidence of its replacement by less hazardous solvents. However, the physical and chemical properties of PAHs vary according to their molecular weight and structure. Their water solubility is low and their octanol/water partition coefficient (K_{ow}) is relatively high (3,37 <log K_{ow}<7,64, Luellen and Shea 2002). This propely provides them an important absorbtion potential on the particles suspended in air or in water. They are chemically stable but are photosensitive. The half-life of these hydrocarbons varies greatly depending on the PAH ; from a few months to several years. Under experimental conditions the half-lives of individual compounds were diversed. In biotic samples half-life of hydrocarbons was in the range of 17 to 126 days. Half-life of PAHs in abiotic sewage sludges was in the range of 32 to 2048 days. The most persistent were benzo(a)pyrene and benzo(b)fluoranthene, respectively. A significant dependence of PAHs' decrease on the presence of microorganisms in sewage sludges after 10 weeks of storage was found (Wlodarczyk-Makula 2012). Several marine animals like fishes metabolize PAH with a cytochrome P_{450} enzyme (AFSSA 2003; Xue and Warshawsky 2005). However, they have been categorized as persistent toxic substances by UNEP (UNEP, 2002).

One of the principal factors in terms of ecotoxicity is the bioconcentration factor (BCF), which is the important criterion in chemicals regulation. It gives an indication that higher in the food chain higher concentrations of a compound are found that may become harmful. Data on individual PAHs, including data on bioaccumulation, are used in risk assessment of (mixtures of) compounds in which PAHs are major components, e.g. oil and oil compounds. As measure for accumulation the bioconcentration factor (BCF) of a compound is used. This is defined as the ratio between the uptake rate of a compound from water into the organism and its elimination rate to water. In the European REACH legislation compounds are divided over three BCF categories: not bioaccumulative (BCF is below 2000), bioaccumulative (BCF is between 2000 and 5000) and very bioaccumulative (BCF is above 5000). Fish are capable of transforming PAHs into compounds that are better soluble in water, which facilitates elimination. This results in lower measured BCF values in fish. Mussels and other invertebrates are much less capable of PAH transformation, which results in higher accumulation of PAHs in these organisms (Bleeker and Verbruggen 2009).

1.1.2.2. Source of polycyclic aromatic hydrocarbons (PAHs)

Mostly, the sources of these substances that are emitted to the environment, consisted of three categories namely; pyrogenic, petrogenic (Grung et al 2016; Qamar *et al* 2017; Gupta 2018) and biological (Wang *et al* 2014; Meade *et al* 2016) (Figure 1.4). In a process well known as pyrolysis, pyrogenic PAHs are composed whenever organic compounds are exposed to high temperatures under low oxygen or anoxic conditions. The destructive distillation of coal into coke and coal tar, dismantling of electronic wastes, combustion of waste printed circuit boards or the thermal cracking of petroleum residuals into lighter hydrocarbons are Pyrolytic (Ortuno *et al* 2014; Cai *et al* 2018) processes that occur intentionally. Meanwhile, other unintentionally processes occur during the incomplete combustion of motor fuels in cars and trucks, the incomplete combustion of wood in forest fires and fireplaces, and the incomplete combustion of fuel oils in heating systems. The temperatures at which the pyrogenic processes occur are ranging from about 350°C to more than 1200°C. Pyrogenic PAHs are generally found in greater concentrations in urban areas and in locations close to major sources of PAHs. In addition, PAHs can also be formed at lower temperatures. It is worth mentioning that crude oils contain PAHs that formed over millions of years at temperatures as low as 100°C – 150°C.

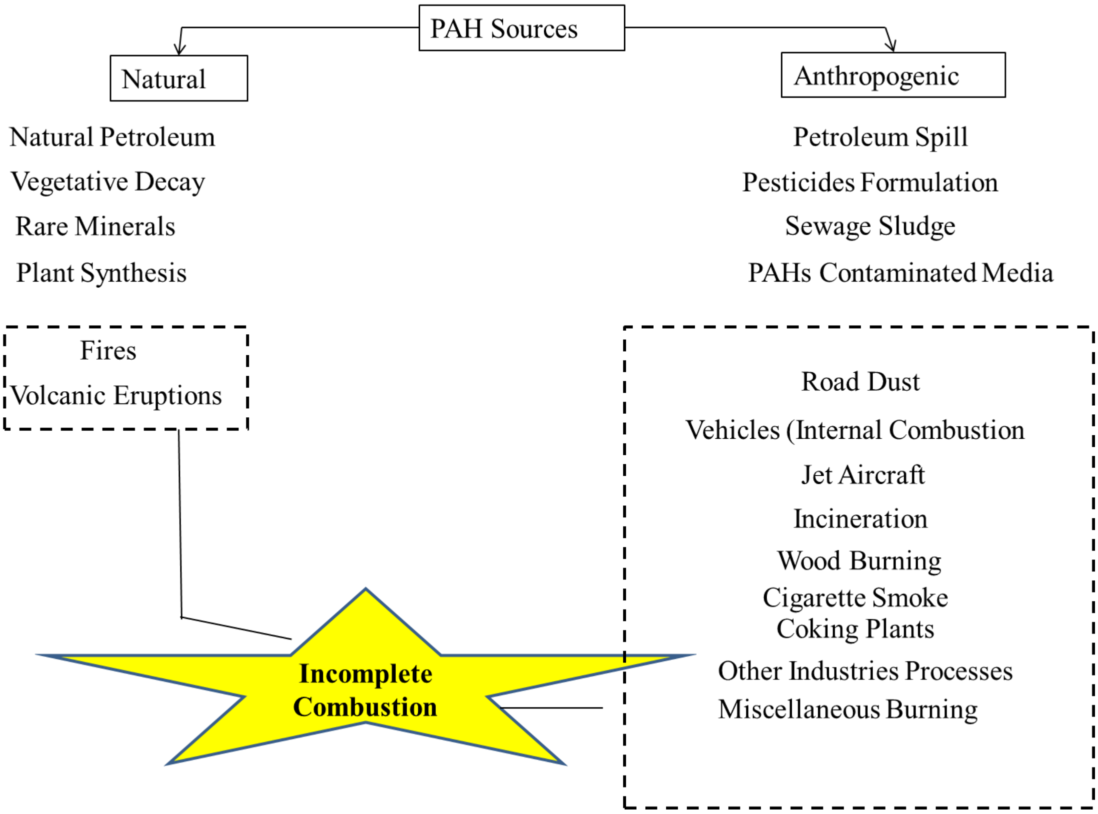


Figure 1.4. Natural and anthropogenic sources of polycyclic aromatic hydrocarbons (PAHs). (Abdel-Shafy and Mansour, 2016).

In this regard, these substances composed during crude oil maturation and similar processes are known petrogenic. This kind petrogenic of these compounds are common because of widespread transportation, storage, and used of crude oil and crude oil products. Mostly, the sources of this petrogenic PAHs encompass oceanic (Beyer *et al* 2016; Brown *et al* 2016; Chen *et al* 2018) and fresh water (Jernelöv 2018) oil spills (Figure 1.5), underground and above ground storage tank leaks, and the accumulation of vast numbers of small releases of gasoline, motor oil, and related substances associated with transportation (Yan *et al* 2015; Keita *et al* 2016 ; Gope *et al* 2018).

Deep Water Horizon Oil Spill, Mexico Bay, US, 2010

Balikpapan Oil Spill, Indonesia, 2018

Figure 1.5. Oil spillage as one of PAHs sources in the marine environment

It is notable that these substances can be composed when the incomplete combustion of organic compounds. These chemicals are discovered in petroleum products as well. Moreover, it is unrecognized that these PAHs could be produced biologically. For instance, these compounds can be synthesized by several vegetation and microbial organisms or composed during the degradation of vegetative matter. The type of these chemicals formation could be both natural and anthropogenic. (Figure 1.4) describes the pattern of PAHs formation.

The formation of PAHs derived from natural sources comprise forest and brush fires, volcanoes, bacterial and algal synthesis, petroleum seeps, erosion of sedimentary rocks containing petroleum hydrocarbons, and the decomposition processes of vegetative fall. On the other hand, the anthropogenic sources of these substances include incomplete combustion such as incinerators and some industrials processes, dispersed sources such as automotive emissions (Cecinato *et al* 2014), smoke from biomass burning (Zhang *et al* 2016), vehicle exhausts, coal combustion (Ma *et al* 2018) cigarette and cigar smoke (Sadeu *et al* 2013; Neal *et al* 2008), and backyard barbecues (Dai *et al* 2018). Other anthropogenic sources of PAHs include petroleum product spills (Uno *et al* 2017; Duan *et al* 2018; Pongpiachan *et al* 2018) sewage sludge (Hu *et al* 2014; Suciu *et al* 2015; Liu *et al* 2018) and tarry or creosote waste materials (Hyötyläinen and Oikari 2004; Gallego *et al* 2008; Bezza *et al* 2016).

1.1.2.3. Use

The major source of PAHs is the incomplete combustion of organic material such as coal, oil and wood. PAHs are not synthesized chemically for industrial purposes. Nevertheless, there are a few commercial uses for many PAHs. They are mostly used as intermediaries in pharmaceuticals, agricultural products, photographic products, thermosetting plastics, lubricating materials, and other chemical industries (Kaminski *et al* 2008). However, the general uses of some PAHs are:

- Acenaphthene: manufacture of pigments, dyes, plastics, pesticides and pharmaceuticals.
- Anthracene: diluent for wood preservatives and manufacture of dyes and pigments.
- Fluoranthene: manufacture of agrochemicals, dyes and pharmaceuticals.
- Fluorene: manufacture of pharmaceuticals, pigments, dyes, pesticides and thermoset plastic.
- Phenanthrene: manufacture of resins and pesticides.
- Pyrene: manufacture of pigments.
- Other PAHs may be contained in asphalt used for the construction of roads, in addition to roofing tar. Furthermore, specific refined products, of precise PAHs, are used also in the field of electronics, functional plastics, and liquid crystals.

1.1.2.4. Transport and Fate of PAHs in the environment

This figure (1.6) describes how PAHs transferred from the sources to human exposition such as inhalation, ingestion directly by dermal contact via air and move to the terrestrial and aquatic environments due to diver processes.

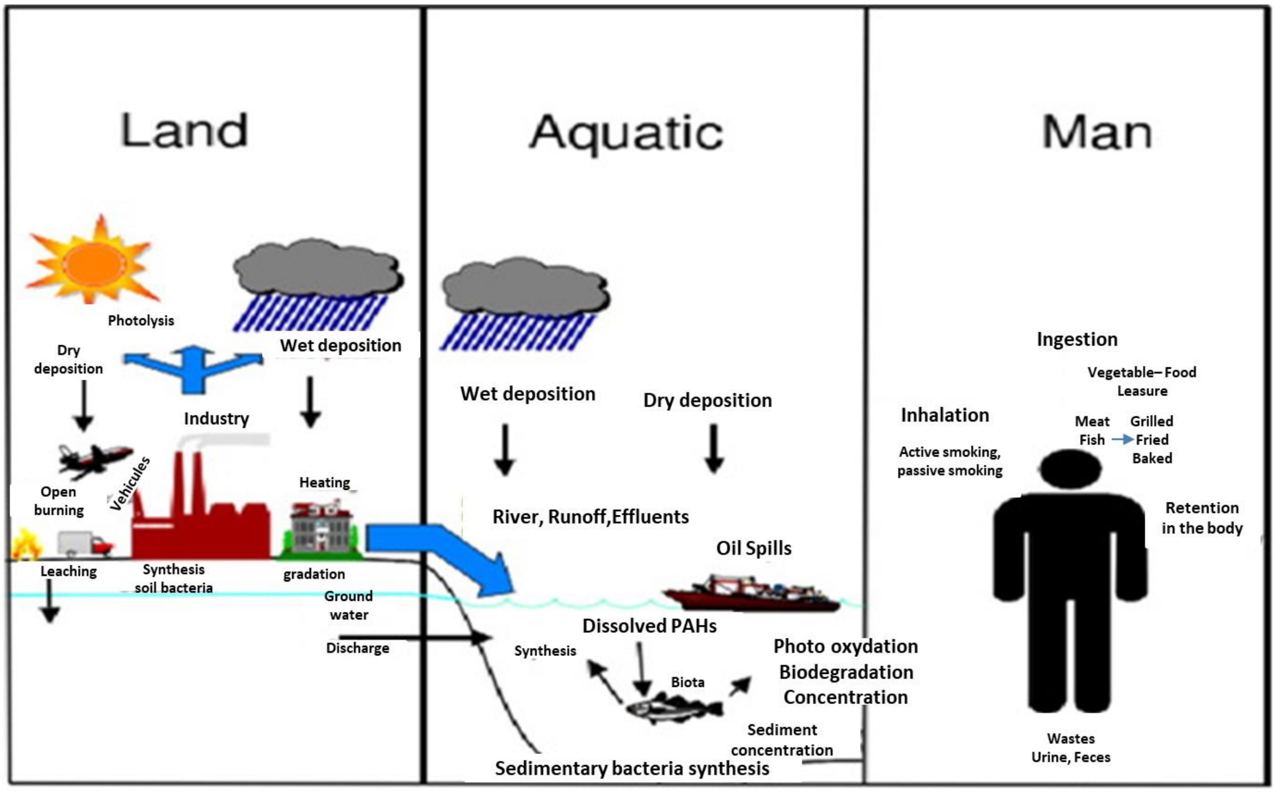


Figure 1.6. Dispersion of PAHs through the air, terrestrial and aquatic environments (Suess, 1976)

Atmospheric emission and deposition of PAHs

The aerial is the principal medium of PAHs are disseminated, it receives a numerous magnitude of these substances induce PAHs becoming ubiquitous within each environmental matrices on earth (Simonich *et al* 2011; Dat *et al* 2017; Gao *et al* 2018; Ma *et al* 2018). They are produced to the aerial media particularly derived from the incomplete combustion of organic matter. The combustion sources could be either natural or anthropogenic. The natural sources include volcanoes and forest fires. Meanwhile, the anthropogenic ones are from vehicle exhaust, agricultural fire, power plants, coke plants, steel plants, foundries and other industrial sources. Mostly, these compounds are discovered in extremely concentrations in the city areas compared to the provincials since the majority of PAHs sources are situated adjacent to the urban centers.

When these PAHs emitted to the aerial, they would become two different phases, a vapor phase and a solid one where the PAHs could be sorbet onto particulate matter (Wang *et al* 2013; Ravindra *et al* 2008; Ohura *et al* 2017). PAHs are categorized as hydrophobic organic substances with low vapor pressures, are likely absorbed to the atmospheric particulate rather than the compounds with higher vapor pressures like benzene. Hydrophobic organic chemicals with low vapor pressures, such as PAHs, are sorbet to atmospheric particulates more readily than chemicals with higher vapor pressures, such as benzene. The divers in vapor pressures of various PAHs compounds induce the individual of these substances disseminated in different concentrations in the vapor (Kameda 2011), and other sorbet phases (Kuo *et al* 2012).

It has been recorded from several works that the magnitude of these substances in the gas phase augment in summer season particularly in tropical zones, on the other hand particulate phase PAHs are predominance during winter generally in Arctic areas (Lai *et al* 2011; Mohanraj *et al* 2012). Furthermore, humidity plays an essential role on the adsorption of these chemicals onto particulate phases (Li *et al* 2011). Besides, the characteristics of suspended particulates play an important role to the adsorption of these chemicals as well such as soot, dust, fly-ash, pyrogenic metal oxides, pollens etc) (Zhang *et al* 2009).

PAHs in surface soils

Aerial PAHs are progressively stored to this planet by dry or wet deposition processes. Several of these chemicals are derived from the adjacent of their sources such as automotive exhaust nearby highway. Many PAHs are from farther sources and have been transferred to diver distances via the air. Meanwhile, PAHs are able to be added to soils if fill materials contain PAHs. Once PAHs are getting stored onto the earth's surface, these compounds would become motile. As these substances deposited in the soil matrices will be bonded to soil particles (Masih and Tanedja 2006; Cachada *et al* 2012), the essential matters effecting PAHs motility of particulates in the subsurface will be adsorbent particle size and the pore throat size of the soils. This pore throat could be meant as the miniscule inter slice between individual grains of soil (Riccardi *et al* 2013).

When the particles where PAHs are getting adsorbent are unable to displace via the soil then the locomotion of PAHs would be restricted since they tend to remain sorbet to particles. The preferences of these substances to be getting adsorbed depend on either the characteristics of these chemicals or the soil. Hence, PAH sorption is one of the processes which may control the soil motility of individual PAHs.

Many works on the interconnection of the partition coefficient with soil characteristics have discovered that the organic carbon content generally produced the high significant correlation (EPRI 2000). The octanol–water partitioning coefficient of PAHs is an essential factor in ascertaining the sorption of these compounds to soils. The octanol–water partitioning coefficient (K_{ow}) has an interrelation to the solubility of an organic compound in water (Schwarzenbach *et al* 1993). The more K_{ow} increases, the more aqueous solubility decreases and the tendency for sorption to a particular soil increase. Nonetheless, the log K_{ow} ($3.37<\log Kow<7.64$) and the low water solubility may affect PAH mobility in soil. There are many factors such as soil conductivity has an important impact on PAHs locomotion as well (Abdel-Shafy and Mansour 2016).

PAHs in sediments

These compounds are stored to the sedimentary environment by similar processes that govern the deposition to surface soils. In rural regions, the PAHs sorbet to atmospheric particles can settle on the surface waters of lakes, streams, and oceans by dry or wet deposition. Therein they are dispersed by water dynamics such as currents, waves, tides and eventually become integrated with the sediment on the bottom area. Furthermore, sediments adjacent to urban activities are affected by atmospheric deposition of PAHs. These sediments also receive inputs of PAHs from storm and sanitary sewer effluents as well as roadway runoff. Eventually, some of the PAHs will be sorbet to particles, settle, and become part of the sedimentary record.

This record has been guided by a few investigators through diagnosing the depositional history in sediment cores to determine tendencies of PAH input into the environment. These cruxes are generally taken in anoxic sediment, in which the absence of oxygen in the water (Tehrani *et al* 2012; EPRI 2015).

When these chemicals are assimilated into sediments they are adequately unmovable due to their non-polar structures repress them from dissolving in water. Nonetheless, PAHs are not completely insoluble, particularly the lower molecular weight PAHs. Thus, discrete magnitudes of these substances do dissolve and become integrated in the pore water in which they would be bioavailable. The existence of pore water organic colloids is able to augment the concentrations of PAHs beyond their aqueous solubility because PAHs will be sorbet onto these organic colloids. These in turn are easily transported through the pore spaces of the sediment. Thus, the sorption to colloids can increase the mobility and bioavailability of PAHs in sediments (Dong *et al* 2012).

1.1.2.5. The Alteration in the Environment

In the environment, particularly, marine area, the hydrocarbons undergo several alteration processes either abiotic (physico-chemical) or biological, often depends on each other which induce the decrease of their concentrations from the initial condition. However, in this work we are barely focusing on the microbial degradation as the most essential regarding the elimination processes of hydrocarbon concentration in the environment.

Biodegradation is an important factor in the removal of hydrocarbons in the nature. Anthropogenic or biogenic hydrocarbons are natural products and there are various microorganisms capable of degrading these substances in the marine environment. These microorganisms are so-called hydrocarbonoclastics. This includes species of the genera *Pseudomoans, Alcanivorax, Acinetobacter, Microccocus, Corynebacteria, Nocardia* and *Rhodococcus*, which are generally known as hydrocarbonoclastic microorganisms (Liu *et al* 2009; Hii *et al* 2009; Bertrand *et al* 2012; Mahjoubi *et al* 2013) which are ubiquitous and very diverse. They are much more numerous in areas that are chronically polluted or have had a rapid and massive influx of oil than in non-contaminated areas. The processes of biodegradation depend on many factors: pH, temperature, concentration of nitrates and phosphates (nutrients), presence of dissolved oxygen, presence of other organic compounds (Bertrand *et al* 2012).

Biodegradation processes depend on many factors such as pH, temperature, concentration of nitrates and phosphates (nutrients, $NaNO_3$ free medium) (Dashti *et al* 2015; Zhao *et al* 2017), presence dissolved oxygen and presence of other organic compounds. (Bertrand *et al* 2012) Generally n-alkanes are the most rapidly biodegraded and then following the branched alkanes. However, cyclanes and aromatics are more resistant to bacterial attacked. On the other hand, PAHs could be degraded by several bacterias such as *Cronbacter sakazakii* which achieved 75.2% and 54.3% phenanthrene and pyrene within 24 h. This bacterium was proven to be rapid and effective in degrading PAHs within 24 h (Umar *et al* 2017). In marine environment, marine-derived fungi (*Trichoderma harzianum, Cladosporium sp*, *Aspergillus sydowii*, *Penicillium citrinum* and *Mucor racemosus*, biodegraded anthracene in 14 days, *Cladosporium sp*. was the most efficient strain and biodegraded more anthracene in the presence (42% biodegradation) than in the absence (26%) of artificial seawater, suggesting that the biodegradation of PAHs may be faster in seawater than in non-saline environment. After 21 days, *Cladosporium sp*. biodegraded anthracene (71% biodegradation), anthrone (100%), anthraquinone (32%), acenaphthene (78%), fluorene (70%), phenanthrene (47%), fluoranthene (52%), pyrene (62%) and nitropyrene (64%) (Birolli *et al* 2018).

Several modes of alkanes and aromatics attacked have been described and involved molecular oxygen (aerobic biodegradation). In the n-alkanes case, the most common mechanism is oxidation of the group terminal methylation leading to the formation of a primary alcohol, an aldehyde and then a carboxylic acid (Cai *et al* 2013). Accordingly, the in vitro aerobic culture lasted 90 days when 99.0% of n-alkanes and 43.03 – 99.9% of PAHs were degraded and the biomarkers and their ratios were changed. The spectra of components in the residual oil showed the similar biodegradation between aerobic process of 90 days and degradation in reservoir which may last for some millions years, and the potential of serious aerobic biodegradation of petroleum in reservoir. 24 Metabolites compounds were separated and identified from aerobic culture, including fatty acid, naphthenic acid, aromatic carboxylic acid, unsaturated acid, alcohols, ketones and aldehydes. The pathways of alkanes and aromatics were proposed, which suggests that oxidation of hydrocarbon to organic acid is an important process in the aerobic biodegradation of petroleum (Cai *et al* 2013).

In certain cases, the oxidation can be ended leading to a dicarboxylic or subterminal acid with formation of a secondary alcohol and then a ketone which is an incorporation of an oxygen atom, is converted into an ester whose hydrolysis leads to an alcohol and an acid. The carboxylic acid formed during primary oxidation is then generally degraded by β-oxidation, but oxidation-type α or ω can also occur (Bertrand and Mille, 1989). On the other hand, other aspects of the biodegradation of hydrocarbons are less well known: exact kinetics of degradation (Birch *et al* 2017; Srivastva *et al* 2017), degradation of asphaltenic structures (Rontani *et al* 1985; Pesarini *et al* 2010), interaction between biodegradation and in particular biodegradation in the absence of oxygen (conditions anaerobic) (Aitken *et al* 2018; Nzila 2018). Bi-, tri-, tetra- and pentacyclic compounds, some of which are considered biogeochemical markers, are also degraded by microorganisms (Saliot *et al* 1988).

1.1.2.6. Toxicity

One of the consequences of PAHs enter into the environment is their toxicities, either in terrestrial area or aquatic ones. These toxicities, particularly toward aquatic organisms (Pie *et al* 2015; Bejarano and Michel 2016; Harvey and Taylor 2017; Cocci *et al* 2018) are induced by several processes such as metabolism or photo-oxydation. Most of them are more toxic when they are exposed to ultra violet light. PAHs have moderate to high acute toxicity to aquatic life and birds (Fritcher *et al* 2002; Luzardo *et al* 2014; McConnell *et al* 2015; Jafarabadi *et al* 2018). In soil matric, these chemicals are unlikely to exert toxic effects on terrestrial invertebrates, unless when the soil is highly contaminated (Snow-Ashbrook 1999; Stroomberg *et al* 2004; Brulle *et al* 2010). Adverse effects on these organisms including reproduction, development, and behavior (Brown *et al* 2016; Bolden *et al* 2017; Boehler et al 2018).

Animals and humans may absorb PAHs through various routes such as inhalation, dermal contact, and ingestion (Beriro *et al* 2016; Franco *et al* 2017; Kadi *et al* 2018 ; Strandberg *et al* 2018 ; Tarafdar and Sinha 2018). On the other hand, plants can absorb PAHs from soils through their roots and translocate them to other plant parts. Uptake rates are generally governed by concentration, water solubility, and their physicochemical state as well as soil type. PAH-induced phytotoxic effects are rare. The representative data explaining this information and the database on this are still restricted. Certain plants contain substances that can protect against PAH effects. Other plants are able to synthesize these chemicals that play an important role as growth hormones (Beyer *et al* 2010). These compounds are fairly persistent in the environment and can be bio-accumulated in marine organisms (Cocci *et al* 2018; Ferrante *et al* 2018). The concentrations of PAHs found in fish and shellfish are expected to be much higher than in the environment from which they were taken. Bioaccumulation has been also shown in terrestrial invertebrates. Nevertheless, metabolism of PAHs is sufficient to prevent bio-magnifications (Inomata *et al* 2012; Tudoran and Putz 2012).

Sese *et al* 2009 worked on the lethalithy, growth and reproduction related to several doses of each PAHs individuals for *C. elegans. A*fter 24 h of exposure to all concentrations of PAH experimental results showed no mortality. However, a concentration-dependent decrease in survival after 72 h of exposure was observed for all 6 PAHs (Tabel 1.1).

Table 1.1. Probit Derived LC_{50} (Lethality), EC_{50} (Growth), and EC_{50} (Reproduction) at 48 h or 72 h of *C. elegans* Exposure to PAHs ($\mu g.l^{-1}$).

PAHs	**48h**			**72h**		
	LC_{50}	**EC_{50}**	**EC_{50}**	**LC_{50}**	**EC_{50}**	**EC_{50}**
	Lethality	**Growth**	**Reproduction**	**Lethality**	**Growth**	**Reproduction**
Acenaphthene	>50,000	>50,000	ND	70,573	>50,000	26,862
Phenanthrene	4772	5568	ND	3758	7085	1214
Anthracene	2561	835	ND	1600	948	880
Fluoranthene	2719	1752	ND	1955	1562	352
Pyrene	2418	792	ND	1653	965	350
Benzo[a]pyrene	174	68	ND	80	96	59

PAH = Polycyclic aromatic hydrocarbon
LC_{50} = lethal concentration
EC_{50} = effective concentration
ND = not detected

Except for acenaphthene (no mortality after 48 h), the pattern of acute toxicity for all the other PAH after 48 h of exposure was similar to that shown for 72 h. Above their LOECs (lowest observed effects concentration) the response slopes for all the PAH were broadly linear. In all cases, LC_{50}

values after 48 or 72 h of exposure were found to be severalfold (acenaphthene, 20-fold ; phenanthrene, 3- to 5-fold ; anthracene, 27- to 43-fold ; fluoranthene, 9- to 13-fold ; pyrene, 12- to 18-fold ; and benzo[a]pyrene, 20- to 45-fold) higher than the aqueous solubility of the respective PAH (Table 1.1). Visual observation indicated that organisms in the control wells (K-medium) continued to develop and were mobile after 72 h of exposure, while there was a marked decline in activity after 24 h, as the concentration of the respective PAH increased across each treatment group (at considerably high concentrations). This may be an indication that the exposed worms might indeed be undergoing stress as a result of exposure to PAH.

Additionally, they studied in context with ecotoxicology endpoints derived for other aquatic invertebrates exposed to PAH : Previous studies on *Daphnia magna, Artemia salina, Chironomus tentans* indicated that high concentrations of PAH (sometimes beyond their respective solubility limits) were also required to produce lethality in 24- to 48-h toxicity tests (Kuwabara *et al* 1980; Le Blanc 1980; Eastmond *et al* 1984; Millemann *et al* 1984; Kagan *et al* 1985; Abernethy *et al* 1986; Suedel 1996; Atienzar *et al* 1999; Spehar *et al* 1999). In comparison with results from this study, C. elegans was approximately 5-fold less sensitive to phenanthrene and 20-fold less sensitive to fluoranthene than *Daphnia magna*. However, the 48-h LC_{50} reported for Daphnia magna (Atienzar *et al* 1999) was similar to that reported in the present study with C. elegans (174 vs. 200 μg.l^{-1}) exposed to benzo[a]pyrene (Table 1.2). Although *C. elegans* showed more sensitivity to benzo[a]pyrene than *Artemia salina* (Kuwabara *et al* 1980; Kagan *et al* 1985), the organism was generally less sensitive to pyrene, fluoranthene, and phenanthrene than *Artemia salina* and *Chironomus tentans.*

Tabel 1.2. LC_{50} Values of PAHs to *C. elegans, D. magna, A. salina*, and *Ch. tentans*

PAHs	Organisms and respective LC_{50} values (μg.l^{-1})			
	C. elegans	*D. magna*	*A. salina*	*Ch. tentans*
Acenaphthene	70.573 (72 h)	41.000 (48 h)	-	-
Phenanthrene	4771 (48 h) 3758 (72 h)	843 (48 h)	677 (24 h)	490 (48 h)
Anthracene	2561 (48 h) 1560 (72 h)	-	50 (24 h)	-
Fluoranthene	2719 (48 h) 1955 (72 h)	117 (48 h)	40 (3 h)	250 (48 h)i
Pyrene	2418 (48 h) 1653 (72 h)	4 (3h) d	8 (3 h)	-
Benzo[a]pyrene	174 (48 h) 80 (72 h)	200 (48 h)	10000 (48 h)	-
Chrysene	-	0.7 (48 h)	-	-

LC_{50} = lethal concentration

Moreover, PAHs are an alarming group of substances for humans and environmental organisms. Many PAHs are carcinogenic, mutagenic, and/or toxic for reproduction (Crone and Tolstoy 2010). Some PAHs are at the same time persistent, bioaccumulative, and toxic for humans and other organisms. Persistent means that the substances remain in the environment for a long time and are hardly decomposed there. Bioaccumulative chemicals accumulate in organisms – including the human body. Substances that combine these three characteristics represent a particular level of concern under an environmental aspect. Experts speak of PBT substances in this context (Persistent, Bioaccumulative, and Toxic substances). If such chemicals are released, they can no longer be removed from the environment due to their characteristics. On the contrary : they accumulate and can harm plants, animals, and ultimately humans.

In terms of hazardous identification, chemists mostly measure the sum total of these 16 compounds to determine the PAH content of products. Benzo[a]pyrene serves as the lead compound, which means it is considered representative of all other PAHs. The idea is that PAHs always occur in mixtures: If benzo[a]pyrene is contained in a substance or product, this typically applies to all other PAHs of concern, which have very similar properties. Benzo[a]pyrene was selected because this compound is particularly carcinogenic. However, there has also been criticism of this reduction of the problem: For example, the Panel on Contaminants in the Food Chain at the European Food Safety Authority (EFSA) submitted a report on PAHs in foodstuffs in 2008 in which they conclude that benzo[a]pyrene alone is not a suitable marker for the presence of PAHs in foodstuffs. According to EFSA, a combination of four specific PAHs is best suited as an indicator of PAH content in foodstuffs. These are benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoroanthene, and chrysene.

Table 1.3. Some select PAHs and their hazard designation

Name	**Melting point (°C)**	**Boiling point (°C)**	**Molecular formula**	**Hazard designation**
Benzo[a]anthracene	170	435	$C_{18}H_{12}$	Hazard : May cause cancer, very toxic to aquatic organisms, with long-term effects
Benzo[b]fluoroanthene	168	481	$C_{20}H_{12}$	Hazard : May cause cancer, very toxic to aquatic organisms, with long-term effects
Benzo[j]fluoroanthene	166	480	$C_{20}H_{12}$	Hazard : May cause cancer, very toxic to aquatic organisms, with long-term effects
Benzo[k]fluoroanthene	217	481	$C_{20}H_{12}$	Hazard : May cause cancer, very toxic to aquatic organisms, with long-term effects
Benzo[a]pyrene	175	495	$C_{20}H_{12}$	Hazard : May cause cancer, may cause genetic defects, impair fertility, and cause harm to the unborn child, very toxic to aquatic organisms, with long-term effects
Benzo[e]pyrene	178	493	$C_{20}H_{12}$	Hazard : May cause cancer, very toxic to aquatic organisms, with long-term effects
Chrysene	255	448	$C_{18}H_{12}$	Hazard : May cause cancer, presumably cause genetic defects, very toxic to aquatic organisms, with long-term effects
Dibenzo[a,h]anthracene	267	524	$C_{22}H_{14}$	Hazard : May cause cancer, very toxic to aquatic organisms, with long-term effects
Naphthaline	80.5	218	$C_{10}H_8$	Warning : May presumably cause cancer, harmful if swallowed, very toxic to aquatic organisms, with long-term effects

German Federal Environment Agency Press Office. Wörlitzer Platz 1, D-06844 Dessau-Roßlau, Germany (2012)

1.1.2.7. The Occurrence of PAHs in Sediments throughout the World (1984 to 2017).

In order to recognize the trend of PAHs concentrations in sediments, we have reviewed 30 scientific articles that have been published around the globe during more than three decades (Table 1.4). We categorized this information into three groups of the periods. In the eras of 1984 to 1999, the concentrations of these chemicals ranged from 0.20 ng.g^{-1} to 310 µg.g$^{-1.}$ The least magnitude of PAHs concentrations was detected in the sediments from North West Region of Arabian Gulf (Al-Asaad 1987) which was connected with the oil refinery and shipping activities. While the highest concentrations were found in Coastal area, Norway which was linked to the heavy industries area and smelter discharged (Naes *et al* 1995). These findings reflect that several places in the world at this era have been heavy contaminated by PAHs. Subsequently, ten years later the concentrations of PAHs declined dramatically with the ranges of 2.2 ng.g^{-1} to 18.381 µg.g^{-1}. The most elevate concentrations of these substances was observed in Coastal Lagoon, Marsala Italia which was categorized as uncontaminated area (Culotta *et al* 2006). This indicates that the occurrence of PAHs in the environment could be derived from the distances through long-range atmospheric transport (LRAT). Whereas, the least concentration was detected in the Gulf of Aden, Yemen which was influenced by harbor, urban and industrial area (Mostafa *et al* 2009). According to several works recently in the last decade, PAHs concentrations in sediments were discovered between 1.1 - 93 ng.g^{-1} and 3079 ng.g^{-1}. The most important concentration was found in Brisbane River, Australia which was linked with urbanized and commercial area (Duodu *et al* 2017). While the lowest one was discovered in West Coast of South Korea, connected with urban and industrial area (Jeon *et al* 2017). Based on this review, we may conclude that the concentrations of PAHs during at least three decades have been undergoing a decrease, particularly in the aquatic area. This also provides a good insight and understanding regarding the mitigation and environmental protection management in the future.

Table 1.4. The Occurrence of PAHs Concentrations in Sediments throughout the World (1984 to 2017)

Land conditions	Concentrations	Locations	References
River discharge, urban and industrial activities	∑PAH 20000 – 1900000 ng.g^{-1}	Naragawest Bay	Pruell and Quinn 1984
Estuary, Urban activities	∑PAH 100 – 1000 ng.g^{-1}	Tamar Estuary, UK	Readman *et al* 1987
Oil refinery activities, shipping	∑PAH 0.20 – 76.25 ng.g^{-1}	North-West region of Arabian Gulf	Al-Asaad 1987
Industrial area and urban	∑PAH 466 - 3354 ng.g^{-1}	Baltic Sea	Lamparczyk *et al* 1988
Urban industrial, transport river discharge	∑PAH 790 – 10.380 ng.g^{-1}	Adriatic Sea	Dujmov and Sucevic 1990
Heavy industries area, smelter discharged	∑PAH 135 – 310 µg.g^{-1}	Coastal area, Norway	Naes *et al* 1995
Oil well areas, oil industries, wastewater discharged	∑PAH 52 - 486 ng.g^{-1}	Industrial area of Kuwait	Saeed *et al* 1996
	∑PAH 6.99 – 8420 ng.g^{-1}dw	France and Spain	Baumards *et al* 1998
Industrial area and urban	∑PAH 17000 ng.g^{-1}	Coastal water, Germany	Witt and Trost 1999
Open sea and near sea	∑PAH 24.7 – 275.4 ng.g^{-1}	South China Sea	Yang 2000
Coastal area	∑PAH 25 - 1450 ng.g^{-1}	Coastal area, France	Soclo *et al* 2000
Shipping, traffic, wastewater discharge	∑PAH 7.6 - 813 ng.g^{-1}	Tododos Santos Bay, B.C Mexico	Macias – Zamora *et al* 2002
High urban and industrial area	∑PAH nd – 12942 ng.g^{-1}	Normandy, France	Cachot *et al* 2006
	∑PAH 6 – 8399 ng.g^{-1}	South China Sea	Boonyatumanond *et al* 2006
Urban industry and harbor area	∑PAH 32 ng.g^{-1} (in protected area) – 13.200 ng.g^{-1}(harbor area)	Northern Adriatic Sea, Croatia	Bihari *et al* 2006
Uncontaminated area	∑PAH 72 - 18381 ng.g^{-1}	Coastal Lagoon, Marsala Italia	Culotta *et al* 2006
Harbor, urban and industrial area	∑PAH 2.2 – 604 ng.g^{-1}	Gulf of Aden, Yemen	Mostafa *et al* 2009
Oil and gas industries, shipping and fishing	∑PAH 200 ng.g^{-1}	Southwestern Barent Sea	Boitsov *et al* 2009
Industrial and agricultural	∑PAH 52.7 - 717 ng.g^{-1}	Pearl River Delta, China	Wang *et al* 2010
Industrial, Fishing	∑PAH nd - 1056 ng.g^{-1}	Lagoon, Northern	Acquavita *et al* 2014

		Adriatic Sea, Italy	
Heavy industrial area	∑PAH 12.9 - 1286 ng.g^{-1}	Kuwait	Lyons *et al* 2015
	∑PAH 0.043 – 0.336 µg.g^{-1} dw	Kapas Island, Trengganu, Malaysia	Chiu *et al* 2015
Wastewater discharged, high amount of urban run-off	∑PAH 203 - 964 ng.g^{-1}	Coastal area, Malaysia	Masood *et al* 2016
Petrochemical industries, agriculture, nuclear power station, aquaculture	∑PAH 340 - 710 ng.g^{-1}	Daya Bay South China	Sun *et al* 2016
Remote area	∑PAH 12.95 – 30.93 ng.g^{-1}	Prydz Bay, Antarctica	Xue *et al* 2016
Oil and gas field, riverine pollutants run-off, agriculture, aquaculture area.	∑PAH 191.99 – 624.44 ng.g^{-1}	Liaodong Bay, China	Zhang *et al* 2016
Urbanized and commercial area	∑PAH 148 - 3079 ng.g^{-1}	Brisbane River, Australia	Duodu *et al* 2017
Urban and industrial area	∑PAH 1.1 - 93 ng.g^{-1}	West Coast of South Korea	Jeon *et al* 2017
Industrial, agricultural, deforestation, tourism	∑PAH 83.2 – 261.7 ng.g^{-1}	Lake in China	Gu *et al* 2017
Riverine sediments	∑PAH 18.40 – 392.29 ng.g^{-1}	Three reservoir of China	Hu *et al* 2017

PAH = Polycylic aromatic hydrocarbon

1.1.2.8. Analytical Methods Review

Through the development of technology, the analytical methods of PAHs have been becoming more and more progress. It is likely correct to state that advances in environmental analysis and assessment has more and less occurred concomitantly with those in analytical methods. A brief diagnosis of accepted and certified methods of analysis of several environmental pollutants suggests that chromatographic techniques play an essential role and probably would be the most widely employed protocols in this field of application. In terms of analytical section, it is important to mention that chromatography is a main technique in the analysis of several environmental matrices such as sediments, soil, air and biological matric to determine these PAHs pollutants. The continued advent of new or improved instrumentation and novel column technologies have meant that chromatography has remained at the forefront in this area of research, and its preeminent position appears unchallenged in the foreseeable future.

In this work, we have reviewed 30 articles (Table 1.5) in which scientist have been working during at least three decades to develop the methods aiming at determining the robustness and the accuracy of the method that would be feasible and reliable to produce a good result. We have categorized these publications into three periods of time in which these scientists had worked. In the eras of 1984 to 1999, soxhlet apparatus become the predominantly of device that was used to extract PAHs from sediments samples (Pruell and Quinn 1984; Al-Asaad 1987; Readman *et al* 1987; Naes *et al* 1995; Saeed *et al* 1996; Lamparczyk *et al* 1998). However, a few other devices such as distillation and MAE with methylene chloride were employed as well (Dujmov and Sucevic 1990; Baumards *et al* 1998). Unfortunately, the recoveries of these methods were unreported. Subsequently, most of the purification processes in this period used alumina silica column to clean up the extracts, eluted by hexane and DCM. Whereas, the identification of PAHs during this first period, scientists employed various devices such as HPLC, GC-FID, UV Fluoroscence spectroscopy and GC/MS.

A decade later, from 2000 to 2010, people have more alternative devices regarding sediment extractions not only soxhlet apparatus (Yang 2000; Culotta *et al* 2006) but also MAE (Cachot *et al* 2006), sonication (Macias – Zamora *et al* 2002) and ASE (Boonyatumanond *et al* 2006; Mostafa *et al* 2009). These extraction methods performed the good recoveries ranged from 60 to 111%. Meanwhile, alumina silica glass column still dominated to clean up these sediment extracts. Nevertheless, there were some investigators used florisil micro-column (Soclo *et al* 2000; Wang *et al* 2010) and glass wool anhydrous (Culotta *et al* 2006). Concerning the separation of these chemicals in sediment samples, GC/MS was the most employed compared to others (Yang 2000; Macias – Zamora *et al* 2002; Boonyatumanond *et al* 2006; Cachot *et al* 2006; Culotta *et al* 2006; Boitsov *et al* 2009; Mostafa *et al* 2009).

Recently, the period from 2014 to 2017, most of scientist still extracts the PAHs from sediments using soxhlet apparatus despite of time and solvents consuming (Acquavita *et al* 2014; Masood *et al* 2016; Xue *et al* 2016; Hu *et al* 2017; Jeon *et al* 2017). A few of investigators used ASE (Zhang *et al* 2016; Duodu *et al* 2017) and ultrasonication (Sun *et al* 2016; Gu *et al* 2017) with a reliable recoveries. Furthermore, the purification of PAHs in the sample extracts predominantly used alumina/silica gel column chromatography beside SPE or florisil column. Considering of analytical step, a 90.9% of the works identified these compounds employing GC/MS in this recent era. Thus, it can be concluded that during three decades, mostly, people employed soxhlet apparatus to extract PAHs in sediment samples and purified the extracts using silica/alumina column to fractionate these chemicals. Whereas, GC/MS, the devices that are being used to separate these substances.

Table 1.5. Review of Analytical Methods Used during 1984 to 2017.

Extraction	Purification	Identification	Performance	References
Soxhlet	Silica gel and elution with hexane/DCM	HPLC		Pruell and Quinn (1984)
Soxhlet with DCM	Alumina column, micro-column of alumina and elution with hexane	HPLC	LOD < 3 ng.g^{-1} dw	Readman *et al* (1987)
Soxhlet	Alumina silica column, elution with pentane and benzene in pentane.	HPLC		Al-Asaad (1987)
Redistillated DCM/Methanol	Alumina column, elution with pentane and DCM	UV Fluoroscence spectroscopy	LOD 0.02 – 0.18 µg.g^{-1} dw	Dujmov and Sucevic (1990)
Soxhlet with cyclohexane	Silica gel column, elution with cyclohexane	GC/FID	LOD 0.5 ng.g^{-1} dw	Naes *et al* (1995)
Soxhlet with hexane/DCM	Alumna silica column, elution with hexane/methylene chloride	GC/MS		Saeed *et al* (1996)
Soxhlet cyclohexane	Alumina column, elution with hexane	GC/FID		Lamparczyk *et al* (1998)
MAE with methylene chloride	Alumina silica column	GC/MS		Baumards *et al* (1998)
Soxhlet with DCM	Alumina silica column	HPLC and Fluorescence detection	Recoveries 70 – 102%	Witt and Trost (1999)
Mechanical stirring extraction,	Florisil micro-column	HPLC		Soclo *et al* (2000)

Chloroform/toluene mixture				
Soxhlet with toluene/methanol	Alumina silica column, elution with pentane and toluene	GC/MS		Yang (2000)
Sonication DCM 3x, solvent exchange to hexane.	Alumina column, elution with pentane/DCM	GC/MS	Recoveries 87 - 111%	Macias – Zamora *et al* (2002)
Microwave Assisted Extraction (DCM)	Silica column, elution with pentane/DCM	GC/MS	Recoveries 80 - 100%	Cachot *et al* (2006)
Redistillated DCM/Methanol		HPLC with Fluoroscence and UV detector	Recoveries 79 – 108%, LOD 0.05 – 0.1 ng.g^{-1}.	Bihari *et al* (2006)
ASE with DCM/ACN	Silica gel column and elution with hexane/DCM	GC/MS	Recoveries 90 – 95%	Boonyatumanond *et al* (2006)
Soxhlet, pentane/DCM	Glass wool, anhydrous Na_2SO_4	GC/MS	Recovery 88%, LOD 0.2 ng.g^{-1}, LOQ 0.7 ng.g^{-1} dw	Culotta *et al* (2006)
ASE, DCM	Alumina silica column, elution with pentane and DCM	GC/MS	Recoveries 60 – 105%, MDL 0.5 – 2.0 ng.g^{-1} dw	Mostafa *et al* (2009)
Saponification in methanolic KOH, followed by extraction with hexane	Silica bond-elute column and the hydrocarbon fractions	GC/MS	LOQ 0.5 ng.g^{-1} dw	Boitsov *et al* (2009)
Extraction Soxhlet, ACN/DCM/n-hexane	Florisil column	GC/MSD	Recoveries 66,2 – 105.7%, S/N of 3	Wang *et al* (2010)
Soxhlet, cyclohexane, then mixture of acetonitrile, acetone, DCM, tetrahydrofurane.	SPME	GC/MS	LOD 1 – 10 ng.g^{-1} dw	Acquavita *et al* (2014)
Saponification in methanolic pottasium hydroxide, liquid-liquide solvents extraction	Drying extract with Na_2SO_4	UV-FS		Lyons *et al* (2015)
Thimble extractor, DCM	Silica gel column, elution with hexane/DCM	GC/MS		Chiu *et al* (2015)
Soxhlet with DCM	Silica gel column	GC/MS	Recoveries 80 – 118%, MDL 0.1 – 1.0 ng.g^{-1}	Masood *et al* (2016)
Ultrasonic bath, hexane/DCM, solvent exchanged to hexane	Florisil glass column, alumina, elution with hexane/DCM	GC/MS	Recoveries 78 – 110%	Sun *et al* (2016)
Soxhlet, DCM solvent exchanged to hexane	Alumina silica column, elution with hexane/DCM	GC/MS	MDL 0.02 – 0.50 ng.g^{-1}	Xue *et al* (2016)
ASE, Acetone and hexane	Silica gel column, florisil and Na_2SO_4	GC/MS	Recoveries 80 – 115%, MDL 0.2 – 4	Zhang *et al* (2016)

			ng.g^{-1} dw	
Soxhlet with DCM	Silica gel column	GC/MSD	Recoveries 75 – 108%, MDL 0.2 – 1.3 ng.g^{-1} dw	Jeon *et al* (2017)
ASE hexane	Clean extract concentrated with Christ-Vacuum concentrator speed dry	GC/MS	Recoveries 61 – 82% LOD 0.01 – 0.21 ng.g^{-1} dw	Duodu *et al* (2017)
Ultrasonication with DCM, solvent exchanged to hexane	Alumina silica column, elution with hexane/DCM	GC/MS	Recoveries 80 – 118%	Gu *et al* (2017)
Soxhlet, DCM	Alumina silica gel column, elution with DCM/n-hexane	GC/MS		Hu *et al* (2017)

DCM = dichloromethane, ACN = acetonitrile, MAE = microwave accelerated extraction, HPLC = high performance liquid chromatography, GC/MS = gaz chromatography/mass spectrophotometry, GC/MSD = gaz chromatography/mass selective detector, GC/FID = gaz chromatography/flame ionization detector. UV FS = ultraviolet flouresence. SPME = Solid phase microextraction, MDL = Method of detection limit, LOD = Limit of detection, LOQ = Limit of quantification.

1.2. Polychlorinated biphenyl (PCBs)

1.2.1. Presentation/Structure/Nomenclature

PCBs are a group of synthetic organic chemical that can induce various dangerous impacts. To date, there are unknown natural sources of these chemicals in the environment. They could be found either oily liquids or solids and are colorless to light yellow. Some PCBs are volatile and may exist as a vapour in the air. They have no known smell or taste. PCBs enter the environment as mixtures containing a variety of individual chlorinated biphenyl components, known as congeners, as well as impurities (EPA, 2000).

Since these compounds are persistent, toxic and bio accumulative, they are categorized as the priority compounds in the list of 12 POPs by the Stockholm Convention in 2008 (so called "the dirty dozen"). Due to the fact that Cortiou creek in Marseilles Bay is one of the important site either ecologically or touristic and lack of the data on PCBs concentrations within sediments, this work is necessary to be carried out.

PCBs are a family of synthetically produced organochlorine compounds and have two phenyl groups which can be substituted by one to ten chlorine atoms (Figure 1.7). The different positions of the chlorine atoms (ortho, meta and para) provides 209 congeners numbered from 1 to 209 by the International Union of Pure and Applied Chemistry (IUPAC). A specific nomenclature, ranging from PCB1 to PC209, was proposed by Ballchmister and Zell (1980). The number and position of the chlorine atoms on the molecule determine both their physicochemical properties and their eco-toxicity. The structural composition of PCBs creates these compounds are particularly stable and have higher degree of chlorination of the molecule lead to the more persistent in the environment. The entire characteristic cause some bioconcentration and fats and biomagnification in living organisms along the food chain.

Moreover, these substances have been widely used in capacitors, transformers, electrical equipment, lubricants and coolants by virtue of their electrical insulating properties, chemical stability and low flammability (U.S. EPA 1999; ATSDR 2000). Their persistence, stability, long-range transport, bioaccumulation and biomagnification ability, as well as toxicity to aquatic life and potential carcinogenicity to higher organisms (Smith *et al* 1999; Persky *et al* 2001; Weintraub and Birnbaum 2008; ATSDR 2011; Su *et al* 2014) arise from features such as halogenation, low vapor pressure (low volatility) and high hydrophobicity (Nicklisch *et al* 2016).

Therefore, these PCBs were categorized as hazard compounds which were adopted by the Aarhus Protocol of 24/06/1998 and by the Stockholm Convention of 2001. Eventually, in this work, we have chosen a group of 7 congeners called PCB indicators (PCBi), was defined on criteria of persistence. These PCB indicators are PCBs 28, 52, 101, 118, 138, 153 and 180 (AFSSA) (Figure 1.8).

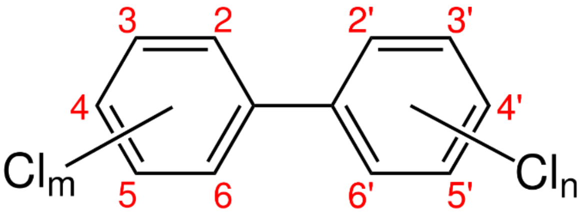


Figure 1.7. Basic PCBs structure (**m** and **n** are for chlorine number and are ranging from 0 to 6)

1.2.2. Physical and chemical properties

Physical and chemical properties of PCBs are summarized in Tabel 1.6

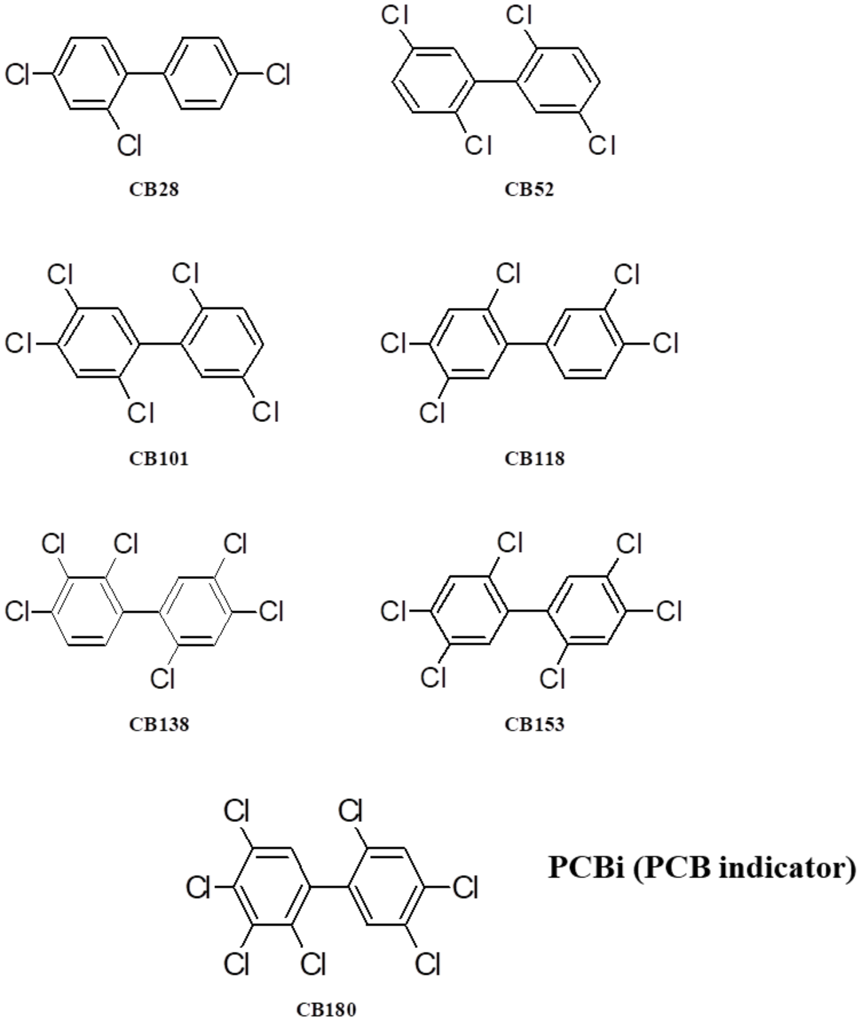
Table 1.6. Physical and Chemical Properties

CAS number	1336-36-3
Formulation	$C_{12}H_{(10-n)}Cl_n$
Molecular weight	200 – 266.5
Color	Clear
Solubility in water	0,10 – 0,59 mg.l^{-1} at (24 - 25°C)
Physical state	oil
Henry Law Constante	2.9 x 10^{-1} – 3.5 x 10^{-3} atm –m^3/mol at 25°C
Boiling point	275 - 366°C
Density	1.18 – 1.38 g.cm^{-3} at 25°C
Log K_{ow}	4.3 – 8.2
Log BCF (Bioconcentration factor)	BCF = 100 000 and 300 000 (OSPARCOM, 2002) Mussel (3.72 – 4.81) Crabs (3.77 – 5.76) Red mullet (3.69 – 5.99) (Porte and Albaiges 1993)
Half-Life	10 – 15 years (Rittel *et al* 2011)

CAS = Chemical Abstracts Service   BCF = Bioconcentration factor

. An important property of PCB is their general inertness; they resist both acids and alkalis and have thermal stability. This made them useful in a wide variety of applications, including dielectric fluids in transformers and capacitors, heat transfer fluids, and lubricants (Afghan and Chau 1989). In general, PCBs are relatively insoluble in water, and the solubility decreases with increased of chlorination. PCBs are also freely soluble in nonpolar organic solvents and biological lipids (EPA, 1980). They are combustible liquids, and the product of combustions are probably more hazardous than material itself. By-products of combustion include hydrogen chloride, polyclorinated dibenzodioxins (PCDDs, and polychlorinated dibenzofurans (PCDFs).

As they are nonpolar, therefore are only slightly soluble. This characteristic inhibits the transport of PCBs from soil to water (ground water or surface water) and makes them bind strongly to soils. PCBs can be transported to surface water via entrainment of contaminated soil particles in surface water runoff. In water, a small portion of PCBs will dissolve, but the majority will bind to organic particles and bottom sediment. Although PCBs have a strong affinity for sediments, small amounts of PCBs are released from sediments to water over time (ATSDR, 2000). Once in the water, PCBs are also taken up by small organisms and fish. PCBs accumulate in the fatty tissue of these organisms. Despite their low volatility, PCBs do volatilize from both, soil and water. This is a result of their widespread presence and extreme stability. With relatively high coefficient of water partition (Log K_{ow}), these substances are easily adsorbed into sediments and soil.



CB28 CB52

CB101 CB118

CB138 CB153

CB180

Figure 1.8. Developed formula of seven PCBs

Moreover, (Rittel *et al* 2011) observed that half-lives of these chemicals are about 10 – 15 years, while OSPARCOM (2002) suggested that PCBs undergo photodegradation in air range from approximately 10 days for a monochlorobiphenyl to 1.5 year for a heptachlorobiphenyl. PCB half-life is about 5 days in water and about 40 days in soil. The persistence of PCBs combined with their high lipophilicity provides the necessary conditions for them to bioaccumulate in living organisms. High bioconcentration factors (between 100 000 and 300 000) as well as high values of the octanol-water partition coefficients (log K_{ow} ranging from 4.3 to 8.2 depending on the congener) have been reported. In fish, the bioconcentration occurs more via the direct uptake from water than through the diet. The chemical properties of PCBs (low water solubility, high stability and semi-volatility) favour their long-range transport in the environment, making them detectable in remote areas like in the Arctic (air, water and organisms) (OSPARCOM 2002).

1.2.3. Use

These chemicals had been using since 1929, however the US banned PCBs manufacturing, processing, distribution and use in 1979 (EIP Associate 1997). The US was responsible for approximately half of the world's production of PCBs and imported approximately 50% of the remainder produced by other countries. PCBs were produced and marketed in the US under the trade names of Aroclor and Pyranol (Nagpal 1992). While in several countries, they use the different names such as Clophen in Germany, Kanechlor in Japan, Fenclor in Italy, Pyralene in France and Soval in USSR. There are no natural sources of PCBs. Although their current commercial use is restricted in the US, they continue to be a common environmental contaminant due to their extremely stability.

The most commonly used Aroclors are 1221, 1232, 1242, 1254 and 1260. These and other Aroclor are used in a variety of materials to enhance insulative properties, improve physical and chemical resistance, and act as plasticizers, coolants and lubricants.

Primary applications of these compounds are used as insulating material, coolant and for fire-resistant properties. Potential sources would be facilities which are used, stored and serviced electrical equipment and which are used the significant amounts of electricity. Other uses of PCBs are in industrial facilities, industrial machinery both fixed and mobile, and consumer products, includes larger power-factor correction capacitors associated with transformers, manufacturing facilities and commercial buildings (usually near high power-usage equipment such as computer rooms and heating and cooling units) ; smaller electric motor-start capacitors that are used in industrial equipment and appliances such as hair dryers, air conditioners, refrigerators, power tools and submersible well pumps, also including capacitors which are used in appliances and electronics such as televisions and microwave ovens.

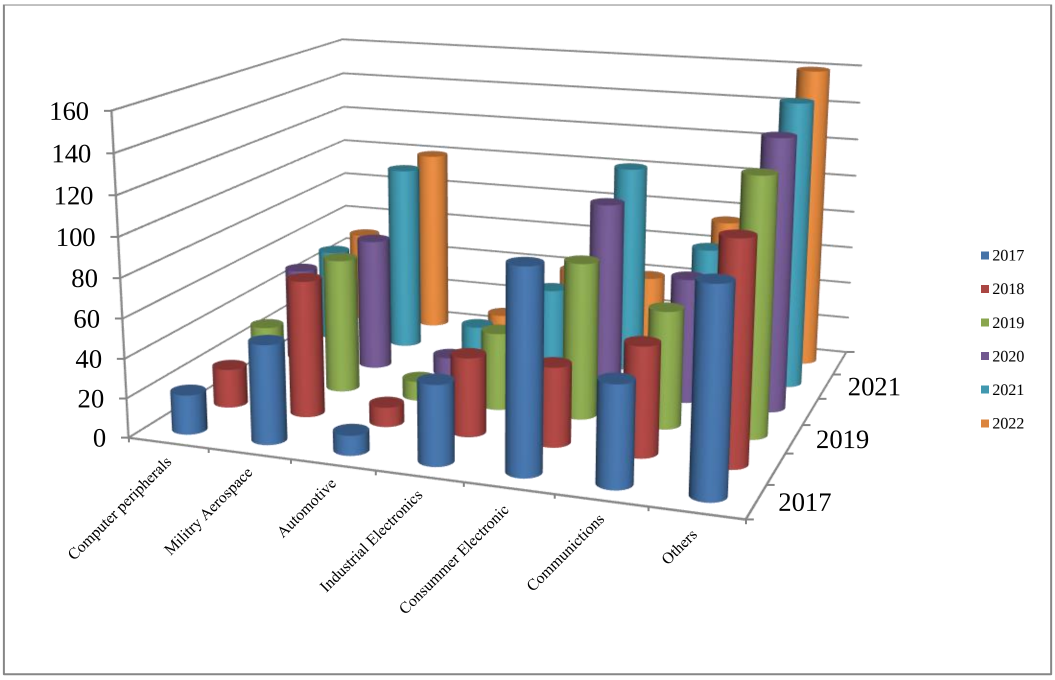


Figure 1.9. PCBs Production Prediction from 2017 to 2022 ($M)

1.2.4. Sources, transport and fate of PCBs in the environment

Marine waters are considered as an important component that playing the role in determining the contaminants transport, fate and sinks in the environment such as persistent organic pollutants (POPs) including PCBs at local and worldwide scales (Wania and Mackay 1996; Dachs *et al* 2002; Jurado *et al* 2007). Prior to the regulation of PCBs under the Toxic Substances Control Act (TSCA) in 1976, PCBs were released (both accidentally and intentionally) into the atmosphere, water and land through sewers, smokestacks, storm-water runoff, spills and direct application to the environment. Large volumes of PCBs have been introduced to the environment through the burning of PCB-containing products, vaporization from PCBs-containing coatings and materials, releases into sewers and streams, improper disposal facilities and by other routes (such as ocean dumping) (ATSDR 2001). Based on the current regulation of PCBs, the current primary « new » sources of PCBs contamination are limited to out dated or illegal landfills and scrap yards and leaks or explosions of electrical equipment and others (such as locomotive transformers) that may still contain PCBs (ATSDR 2001). Other sources are facilities or sites that were previously contaminated with PCBs are emitted and re-deposited to the environment via volatilization from water and soil, wet and dry depositions, and re-volatilization (*Hazardous Substances Data Bank*, HSDB 2003)

PCBs could be released into the environment from the sources as mentioned above through various mediums. Therefore, these substances have been detected in the different environmental matrices from various area throughout the globe. In the sediments (Fu *et al* 2006; Bettinetti *et al* 2016; Oziolor *et al* 2018) in soil (Kuzu *et al* 2016; Cetin *et al* 2017; Dumanoglu *et al* 2017; Pokhrel *et al* 2018) in aerosols (Kuzu *et al* 2016; Lyng *et al* 2016; Melymuk *et al* 2016; Dumanoglu *et al* 2017) and in biota (Bettinetti *et al* 2016; Stuart-Smith and Jepson 2017; Oziolor *et al* 2018). However, PCBs are generally more deposited in soil compared to other mediums (Cetin *et al* 2017).

Model study revealed the interconnection among several components such as soil, sediments, water, fish and air as the mediums where PCBs are transported in the river. A model has been developed and indicated that fish and sediments represent environmental compartments with the highest PCBs concentrations (Lu *et al* 2015). Nevertheless, the greatest mass of PCBs (over 70%) is likely to remain in the soil. As emissions decline, soil could then act as a significant secondary source of PCBs with the river bed-sediment functioning as a long-term reservoir of PCBs. They also mentioned that the most significant result was a tendency for climate change to enhance the evaporation of PCBs from soil to air. Therefore, PCBs as one of the persistent organic pollutants (POPs) are potential to be long-range transport (Lohmann *et al* 2007; Urbaniak 2007; Lu *et al* 2016).

However, sediments are not always being guarantee as a secure repository for contaminants. The alteration in external conditions (*e.g.,* climate) in the sediments and the internal physical and biogeochemical conditions in the sediments and dredging spoil (*e.g.*, pH, salinity and redox potential) could result in particles and dissolved contaminants being mobilized and entering the overlying water (Förstner *et al* 1984; Stigliani 1988; Chester 1993; Williams *et al* 1994; Pakhomova *et al* 2007; Vink *et al* 2010 a,b ; Laane *et al* 2013).

The existence of these hydrophobic and semi-volatile substances is of a particularly interest because of their ubiquity, toxicity and accumulation in the components of food webs (Jones and de Voogt 1999; Jurado *et al* 2007). It was well-explained that water column dynamics have a significant impact on the air-sea exchanged of these compounds, as their efficient removal from the mixed surface layer decreases the volatilization rates and captures atmospheric pollutants (Dachs *et al* 1999; Scheringer *et al* 2004; Jurado *et al* 2007).

1.2.5. The Alteration in the Environment

Polychlorinated biphenyls are persistent in the environment but also have the ability to naturally biodegrade over time. Once PCBs reach sediment, there is opportunity for dechlorination and degradation to occur.

There were various bacteria encountered in sediments both aerobic and anaerobic which belonging to the genera *Burkholderia, Pseudomonas, Sphingomonas, Rhodococcus, Norcardia, Arthrobacter, Acinetobacter, Bacillus* and *Corynebacterium* (Seto *et al* 1996; Sakai *et al* 2005), exemplify abilities to dechlorinate and biodegrade PCBs (Song *et al* 2015). Aerobic bacteria are found on the surface of sediment in an oxygenated environment. Aerobic bacteria are able to break open the biphenyl ring by attacking the 2,3 position on a ring with 2 oxygen atoms. The ring is broken, producing a p-chlorobenzoic acid. Through this degradation process, aerobic bacteria virtually have the ability to fully eliminate PCBs. Aerobic microbial degradation is often possible only when halogenated compounds have a maximum of four-to-five halogen atoms, although an aerobic bacterium responsible for deca-BDE debromination was isolated from sediment (Deng *et al* 2011).

On the other hand, some aerobic bacteria are able to degrade highly chlorinated PCB congeners using an initial oxygenase reaction (Sobiecka *et al* 2009; Nabavi *et al* 2013). The results of the study showed the average removal percentage of PCB compounds under aerobic conditions was about 50%. Adebusoye *et al* (2008); Nabavi *et al* (2013) reported 37% degradation of Aroclor 1242 from transformer oil in aerobic condition. Comparison of degradation rate of Aroclors showed the highest average removal percentage for Aroclor 1242 with a value of 85.4% in anaerobic reactor. Quesen et al. also reported extensive dechlorination of Aroclor 1242 and 1248 in comparison with Aroclors

1254 and 1260 (Borja *et al* 2005). Some microorganisms were more capable of metabolizing high-chlorinated Aroclors under anaerobic conditions than aerobic conditions. Although only few studies report the use of biofilm to degrade PCBs (Mukerjee-Dhar et al1998; Kuncova et al 2002; Borja *et al* 2006), application of biofilms as an alternative in the degradation of PCBs offers some advantages such as the presence of large microbial diversity in a stable form (Borja *et al* 2006).

In conclusion, degradation and dechlorination of PCBs occurs in sediment by the actions of aerobic and anaerobic bacteria (Demirtepe *et al* 2015; Cao *et al* 2018; Kaya *et al* 2018). Limitations of both processes leave complete removal of PCBs from sediment unrealistic. Both aerobic and anaerobic bacteria effectiveness is dependent on chlorines positions and overall chlorination. Anaerobic bacteria fail to remove any ortho positioned chlorine atoms, but show great potential in the removal of meta and para chlorines. Dechlorination is congener and concentration dependent. Unfortunately, PCB's were released into waterways over 30 years ago ; the chemicals have become dispersed at low concentrations due to tides, river flows, flooding, and weathering, hindering potential for dechlorination. It is also difficult to document exact dechlorination rates within nature, due to PCB concentrations decreasing in sediment because of absorption into other media. As PCBs have are dechlorinated, they are also dissolved into water, volatized into air, and are been ingested by marine life (Grilo *et al* 2014; Pei *et al* 2017). The presence of daughter congeners in sediment samples will be a good indication of dechlorination and allow back tracking to determine to original Aroclor mixture. Knowing patterns of dechlorination will also allow congener patterns to be established for the marine food web (Weijs *et al* 2011; Torres *et al* 2016).

1.2.6. Toxicity

PCBs are categorized as persistent organic pollutants (POPs) which are most widespread dispersed. They are continuously employed worldwide in industrial application. These compounds are synthetic, ubiquitous, hydrophopic, and persistent as their environmental half-life ranges from years to several decades or more. They are semi volatile and display high chemical, thermal stability and high resistance to biodegradation. Furthermore, these chemicals undergo Long-Range Atmospheric Transport (LRAT) and deposition in the open sea (Wania and Mackay 1993; Wania 2003).

Number of scientific publications have revealed that human health could be endangered by these chemicals via respiratory and cardiovascular disease (Chen *et al* 2016; Fang *et al* 2016; Dziubanek *et al* 2017). Additionally, terrestrial animals, marine fishes, invertebrates, turtles and others biota have been contaminated by these PCBs in Spain, Germany, Canada, Croatia, USA, Norway and Turkey (Gagnon *et al* 1990; Huhnerfus *et al* 1995; Burton *et al* 2012; Roiget *et al* 2012; Cheng *et al* 2013 Delistraty, 2013 Asselman *et al* 2014; Salice *et al* 2014; Samuelsson *et al* 2015; Dhams *et al* 2016; Dikmen *et al* 2016; Milun *et al* 2016; Han and Currell 2017). Therefore, in order to be able to abate the adverse effects of human exposure to PCBs, the residential waste burning should be totally banned and the awareness of the health risk associated with the PCBs inhalation exposure should be raised in the society.

According to the toxicological distribution dynamic, these substances can be divided into two categories. Firstly, the dioxin-like coplanar PCBs (DL-PCBs) which are able to activate the aryl hydrocarbon receptor (AhR) and this is suggested their principle mode of action (Van den Berg *et al* 2006). Conversely, the majority of abundant environmental non-dioxin-like PCBs (NDL-PCBs) do not activate the AhR, and there is no generally accepted risk concept for these chemicals (Hamers *et al* 2011), Even though several NDL-PCBs have been suggested to inhibit the AhR transcriptional activity (Ovesen *et al* 2011; Brenerová *et al* 2016). However, NDL-PCBs influence numerous special type of action related with carcinogenicity, neurotoxicity or endocrine disruption (Grandjean and Landrigan 2006; Lauby-Secretan *et al* 2013; Gore *et al* 2015). They have been illustrated i) to interact with nuclear receptors controlling metabolism of both endogenous and exogenous compounds (including hormones), such as constitutive androstane receptor (CAR) or pregnant X receptor (PXR) ; ii) to directly modulate gene expression dependent on activation of estrogen (ER), androgen (AR) or thyroid receptors; iii) to provide effects connected with carcinogenesis/tumor promotion, such as generation of reactive oxygen species (ROS) or inhibition of gap junction intercellular communication (GJIC); or to produce neurotoxic effects (Machala *et al* 2003; Knerr and Schrenk 2006; Pessah *et al* 2006; Simon *et al* 2007; Hamers *et al* 2011; Gore *et al* 2015; Grimm *et al* 2015). Effects of NDL-PCBs can also be linked with further alterations of physiological processes within the body, as illustrated in case of disruption of CAR/PXR signaling by PCBs, linked with deregulation of energy metabolism, inflammation and liver diseases (Dutta *et al* 2008; Wahlang *et al* 2017; 2016).

Furthermore, the toxicological properties of PCBs are affected by the number and position of the chlorine atoms, as substitution in the ortho position hinders the rotation of the rings. PCBs without ortho substitution are generally referred to as coplanar and all others as non-coplanar. Coplanar PCBs can bind to the Ah receptor and may exert additional effects, which are not observed with non-coplanar PCBs. PCBs have a low acute toxicity to laboratory animals, with acute LD_{50} values in rats in the range of 2 to 10 $g.kg^{-1}$ body weight. Effects are manifested primarily through chronic exposure. Effects on the liver, skin, immune system, reproductive system, gastrointestinal tract and thyroid gland have been observed associated with exposure to PCB mixtures or individual congeners. PCBs are classified by IARC as probable human carcinogens (group 2A) with adverse effects being predominantly linked to high blood concentrations. A maximum daily intake of 0.2 $µg.kg^{-1}$ body weight has been proposed by IPCS (1993) (OSPARCOM 2002).

PCBs are toxic to aquatic organisms, with 96-hour LC_{50} values in the range of 0.015 $mg.l^{-1}$ in fathead minnows to 2.74 $mg.l^{-1}$ in bluegills. PCBs have a low acute toxicity to birds, with 5-day dietary LC_{50} values in the range of 747 $mg.kg^{-1}$ diet in quail to more than 5 $g.kg^{-1}$ in several other species. There is growing evidence, which associates PCBs to reproductive and immunotoxic effects in wildlife. In laboratory studies, NOELs (No-observed effect levels) values for these effects in monkeys vary between 30 and 100 $µg.kg^{-1}$ body weight (OSPARCOM 2002).

1.2.7. Occurrence of PCBs in sediments throughout the world

We have reviewed 30 articles that have been published on various journal during three decades as listed below (Table 1.7). Since 1985 to 2008, the concentration levels of $\sum$ PCBs in marine and river sediments ranged between 0.006 to 1648 $ng.g^{-1}$. The most elevated concentration was found at Ionian Sea, Southern Italy from harbor activities as the punctual pollution (Cordellicchio *et al* 2007). Whereas the lowest one was recorded at the aquatic ecosystem in Hongkong which was connected with local industry, agriculture and domestic sewage (Kannan *et al* 1989). It is interesting that these compounds were detected at the deep sea as of 130 $ng.g^{-1}$ at the Gulf of Main (Larsen 1985) and of 6 – 65 $ng.g^{-1}$ at the North Green Land (Kjolholt and Hansen 1986). At the remmote area where the region was chategorized as uncontaminated area at Berring Sea and the Gulf of Alaska, PCBs still detected. This suggested that PCBs are persistence and long-range transpor properties (Yu *et al* 2007; Rezaei *et al* 2008; Fang *et al* 2011; Li *et al* 2012).

In 2010 to 2017, the occurrence of these chemicals in the sediments recorded between 0.0039 and 1232 $ng.g^{-1}$. The highest concentration was found at Jobos Bay, Puerto Rico which was linked with urban and industrial area (Alegria *et al* 2016). Whereas the lowest one was found at Chao River in China where was not connected with urban and industrial area. This suggested that PCBs were recorded not only at the area directly connected with the potential sources but also at a long distance location due to their persistence and long-range transport properties as we explained earlier. Additionally, an evidence that Brazilia as a developing country is the most using PCBs as the important raw materials in terms of industry.

Tabel 1.7. Occurrence of PCBs in sediments throughout the world (1985 to 2017)

Sources	**Concentrations**	**Locations**	**References**
Deep Sea sediment	∑ PCBs (130 µg.kg^{-1})	Gulf of Maine	Larsen *et al* (1985)
Depth sediments	∑ PCBs (6 - 65 µg.kg^{-1})	North Green Land	Kjolholt and Hansen (1986)
Harbor area	∑ PCBs (7.2 – 81 µg.kg^{-1})	Waukagen Harbor, US	Swackhamer and Armstrong (1988)
Local industry, agricultural, and domestic sewage	∑ PCBs (0.006 – 2.2 µg.kg^{-1})	Aquatic ecosystem, Hongkong	Kannan *et al* (1989)
Tourist, agriculture, industrial area	∑ PCBs (0.05 – 9.69 µg.kg^{-1})	Alicante, Spain	Prats *et al* (1992)
Urban and industrial site	∑ PCBs (2 – 116 µg.kg^{-1})	Essex Coast,	Scrimshaw *et al* (1994)
Uncontaminated area	∑ PCBs (0.13 – 2 µg.kg^{-1})	Bering Sea and Gulf of Alaska	Iwata *et al* (1994)
Agriculture and industrial area	∑ PCBs (0.47 – 28.1 µg.kg^{-1})	Coast of North Vietnam	Nhan *et al* (1999)
Urban, industry and agriculture	∑ PCBs (55.9 – 860 µg.kg^{-1})	South East Regional Park, Madrid, Spain	Fernandez *et al* (2000)
Agriculture and industrial waste	∑ PCBs (116 - 304 µg.kg^{-1})	California, US	Spozhnikova *et al* (2004)
Sewage sludge input from the river	∑ PCBs (6.5 – 32.9 µg.kg^{-1})	Coastal Sea of Qing Dao, China	Pan *et al* (2007)
Harbor activities	∑ PCBs (2 - 1648 µg.kg^{-1})	Ionian Sea, Southern Italy	Cordellicchio *et al* (2007)
Industrial effluents, petroleum refineries, petrochemical plants	∑ PCBs (184.16 µg.kg^{-1})	Guanaba Bay, Rio de Jeneiro, Brazil	Santos de Souza *et al* (2008)
Sewage discharged without treatment	∑ PCBs (1.3 – 384 µg.kg^{-1})		Hoai *et al* (2010)
Entrance river, aquaculture area, slightly human activities	∑ PCBs (0.91 – 6.48 µg.kg^{-1})	Bay Yangdian Lake, North China	Dai *et al* (2011)
Harbor, urban runoff, effluent from sewages	∑ PCBs(62 – 601 µg.kg^{-1})	Port of Spain, Trinidad and Tobago	Mohammed *et al* (2011)
Industrial, agricultural, urban effluents	∑ PCBs (0.20 – 1.92 µg.kg^{-1})	Mediterranean Coast, Egypt	Aly Salem *et al* (2013)
Agricultural area	∑ PCBs (0.0039 – 0.0365 µg.kg^{-1})	Chao River, China	Yu *et al* (2014)
Industrial area, chemical industry, food and agriculture	∑ PCBs (2.8 - 435 µg.kg^{-1})	Huveaune River, France	Kanzari *et al* (2014)
Industry, advanced agriculture, high populated	∑ PCBs (1.08 – 3.5 µg.kg^{-1})	Coast of Korea	Choi *et al* (2014)
Agricultural area20	∑ PCBs (0.6 – 35.6 µg.kg^{-1})	The Canang Island, Spain	Luzardo *et al* (2014)
Industrialization and oil refined	∑ PCBs (1.25 – 78.4 µg.kg^{-1})	State of Kuwait	Lyons *et al* (2015)
Urban and industrial area	∑ PCBs (0.42 - 1232 µg.kg^{-1})	Jobos Bay, Puerto	Alegria *et al* (2016)

		Rico	
Industrialization, urbanization, agriculture	∑ PCBs (17.68 – 169.26 µg.kg^{-1})	Pearl River Estuary, China	Zhao *et al* (2016)
Fishery and harbor activities, high population	∑ PCBs (0.54 – 55.5 µg.kg^{-1})	Shantou Bay, China	Shi *et al* (2016)
Industrial, petroleum, urban, agricultural	∑ PCBs (0.22 µg.kg^{-1})	Red Sea Coast, Egypt	Ragab *et al* (2016)
Metallurgic industry urban and high population	∑ PCBs (0.59 – 12.38 µg.kg^{-1})	Songhua River, China	Cui *et al* (2016)
Urban and industrial port, associated with anthropogenic activties	∑ PCBs (0.61 – 17.6 µg.kg^{-1})	Buenos Aires, Argentine	Tombesi *et al* (2017)
Deep water sediments	∑ PCBs (0.3 – 7.7µg.kg^{-1})	Levantine Basin, SE Mediterranean	Astrahan *et al* (2017)
Industrial and urban area	∑ PCBs (0.54 – 16.6 µg.kg^{-1})	Liaohe Estuary, China	Li *et al* (2017)
Industrial and urban area	∑ PCBs (<DL – 5.87 µg.kg^{-1})	Estuary of Babytonga Bay, Brazil	Rizzi *et al* (2017)
Ship dock ballast sediment	∑ PCBs (115.18 – 574.91 µg.kg^{-1})	Jiangyin, China	Su *et al* (2017)

PCB = Polychlorinated byphenil

1.2.8. Review of Analytical Methods

PCBs have garnered wide attention of scientific and legislative communities in several decades due to their wide spread presence in the environment, either in sediments, air, water, or in the biota. They are generally considered to be stable in the environmental and the biological systems, and have been shown to be correlated with congeners of toxicological relevance.

The analytical methods and techniques which are employed to detect and to measure the PCBs in environmental matrices vary. This is due to the complexity of these matrices and the broad range of PCBs pollutants that have been found. However, sediments matrices are the most interested medium to be studied in terms of PCBs contamination. We have reviewed 32 articles that have been published in several journals throughout the world concerning analytical methods used to determine these compounds in sediments (Table1.8).

During one and a half decades (1985 to 2000), most of PCBs extraction used soxhlet apparatus with excellent recoveries which were ranged between 64 to 113% (Kjolholt and Hansen 1986; Swackhamer and Armstrong 1988; Prats *et al* 1992; Glynn *et al* 1995; Nhan *et al* 1999; Fernandez *et al* 2000). While alumina silica gel column dominated the clean-up procedure of these chemicals (Swackhamer and Armstrong 1988; Kannan *et al* 1989; Prats *et al* 1992; Scrimshaw *et al* 1994; Nhan *et al* 1999; Fernandez *et al* 2000). The investigators identified these substances using two devices which were GC/ECD (Kjolholt and Hansen 1986; Prats *et al* 1992; Glynn *et al* 1995; Fernandez *et al* 2000) and GC/MS (Scrimshaw *et al* 1994; Kannan *et al* 1989; Swackhamer and Armstrong 1988; Larsen *et al* 1985) to separate the PCBs from sediments matrices. A decade later, the extraction of PCBs still used soxhlet apparatus (Spozhnikova *et al* 2004; Cordellicchio et al 2007; Santos de Souza et al 2008; Dai *et al* 2011; Mohammed *et al* 2011; Aly Salem *et al* 2013; Choi *et al* 2014; Luzardo *et al* 2014; Yu *et al* 2014) as the preference device beside ASE (Conka *et al* 2014; Kanzari *et al* 2014) and other instruments despite of solvents and time consuming with good recoveries of 70 to 125%. Concerning clean-up, in this period, people used silica alumina glass column (Cordellicchio *et al* 2007; Pan *et al* 2007; Santos de Souza *et al* 2008) and some of them used florisil (Spozhnikova *et al* 2004; Hoai *et al* 2010; Dai *et al* 2011; Mohammed *et al* 2011; Aly Salem et al 2013; Choi *et al* 2014). The investigators identified these PCBs used GC/ECD (Spozhnikova *et al* 2004; Cordellicchio *et al* 2007; Santos de Souza *et al* 2008; Dai *et al* 2011; Mohammed *et al* 2011; Aly Salem *et al* 2013; Choi et al 2014; Kanzari *et al* 2014; Yu *et al* 2014) beside GC/MS and others with accurately results.

Recently, people still used similar devices to analyze PCBs in sediments as they did in the previous decades. Soxhlet apparatus was still preferred to employed to extract these compounds with excellent recoveries (Lyons *et al* 2015; Alegria *et al* 2016; Cui *et al* 2016; Ragab *et al* 2016; Shi *et al* 2016; Li *et al* 2017; Rizzi *et al* 2017). However, some investigators still used ASE and Ultrasonication (Zhao *et al* 2016; Su *et al* 2017). Considering purification, alumina silica glass column dominated this analysis to separate PCBs in the sediment samples (Lyons *et al* 2015; Cui *et al* 2016; Shi *et al* 2016; Zhao *et al* 2016; Li *et al* 2017; Rizzi *et al* 2017). These days, the identification of PCBs are using various devices such as GC/ECD, GC/MS and GC/MS/MS. The last one is the most sophisticated with highest accurately detection.

Table 1.8. Review of Analytical Methods used (1985 to 2017)

Extraction	**Purification**	**Identification**	**Performance**	**References**
Shaker	Tetrabuthyle ammonia sulphate to remove sulfur	GC/MS		Larsen *et al* 1985
Soxhlet (Acetone/hexane)	Florisil column, elution with hexane	GC/ECD		Kjolholt and Hansen 1986
Soxhlet (Acetone/hexane), solvent exchanged to hexane	Alumina silica gel column, elution with hexane	GC/MS	Recovery (93%)	Swackhamer and Armstrong 1988
Mechanical Shaker (hexane)	Silica gel glass column, elution with hexane/DCM	GC/MS		Kannan *et al* 1989
Soxhlet (hexane)	Silica gel column fractionation	GC/ECD	Recovery >90%	Prats *et al* 1992
Shaker, hexane by end-over-end	Alumina column, elution with n-hexane	GC/MS	Recovery (64%) LOD (1.0 ng.g^{-1})	Scrimshaw *et al* 1994
Soxhlet, Acetone/methylene chloride	Methylene Chloride – Alumina, pre-clean, methylene chloride-gel permeation chromato	GC/ECD	Recoveries (40 – 113%), MDL (1 ppb)	Glynn *et al* 1995
Soxhlet (hexane)	Silica gel column fractionation	GC/ECD		Nhan *et al* 1999
Soxhlet (Toluene)	Alumina silica column	GC/ECD	Recoveries (81 – 94%), MDL (0.2 – 10 ng.g^{-1})	Fernandez *et al* 2000
Soxhlet (Acetone/hexane)	Florisil cartridge	GC/ECD	Recoveries (70 – 101%), MDL (0,1 – 0.34 µg.kg^{-1})	Spozhnikova *et al* 2004
ASE (toluene), exchanged solvent to hexane	Multilayer silica gel column, elution with hexane	HRGC - HRMS	Recoveries (40 – 93%)	Pan *et al* 2007
Soxhlet (Acetone/hexane)	Silica gel column, elution with hexane/DCM	GC/ECD	Recovery (>75%) LOD (2.5 µg.kg^{-1})	Cordellicchio *et al* 2007

Soxhlet (Acetone/hexane/isooctane)	Silica column fractionation, elution with n-hexane	GC/ECD		Santos de Souza *et al* 2008
Ultrasonic extraction (Acetone/n-hexane)	Florisil cartridge, elution with acetone/hexane	GC/EI/MS	Recoveries (72 – 121%), LOQ (0,6 ng.g^{-1})	Hoai *et al* 2010
Soxhlet (Acetone/hexane)	Florisil wet column, elution with hexane	GC/MS	Recoveries (68 – 88%), LOD (0.06 – 0.32 ng.g^{-1})	Dai *et al* 2011
Soxhlet (DCM)	Florisil column	GC/ECD	Recoveries 70 – 114%)	Mohammed *et al* 2011
Soxhlet (hexane)	Glass column florisil, elution with hexane	GC/ECD	Recoveries (97 – 113%)	Aly Salem *et al* 2013
ASE (toluene), exchanged solvent to hexane	Silica alumina column, elution with hexane	HRGC - HRMS		Conka *et al* 2014
ASE (Acetone/hexane)	Slica gel glass column	GC/MS	Recoveries (78 – 125%), LOD (0,006 – 1 ng.g^{-1})	Kanzari *et al* 2014
Soxhlet (Acetone/hexane)	Silica alumina column, florisil cleanup	GC/ECD	Recoveries (75 – 114%), MDL (0.01 – 0.03 ng.g^{-1})	Choi *et al* 2014
Soxhlet,	Purification step using gel permeation chromatography (GPC)	GC/MS/MS	Recoveries (74 – 104%)	Luzardo *et al* 2014
Soxhlet (Acetone/hexane)	Alumina silica gel column, elution with hexane/DCM	GC/MS		Yu *et al* 2014
Soxhlet (Acetone/hexane)	Silica alumina column, elution with acetone/hexane	GC/ECD		Lyons *et al* 2015
Soxhlet (DCM)	Column florisil, elution with DCM then hexane	GC/MS	Recoveries (87 – 104%)	Alegria *et al* 2016
ASE (hexane/Acetone)	Silica gel column, Na2SO4 to clean the extract	GC-ECD	Recoveries (80 – 112%)	Zhao *et al* 2016
Soxhlet (Acetone/hexane/DCM	Alumina silica gel column, elution with hexane/DCM	GC/ECD	Recoveries (82 – 103%)	Shi *et al* 2016
Soxhlet (hexane/DCM)	Florisil glass column, elution with hexane	GC/MS	Recoveries 91 – 104%)	Ragab *et al* 2016
Soxhlet (Acetone/hexane)	Silica gel column fractionation, elution with n-hexane/DCM	GC/MSD	Recoveries 75 – 118%), MDL (3 - 32 ng.kg^{-1})	Cui *et al* 2016
Automatic extractor B8-11 Buchi System (DCM)	Glass column sulfuric acid modified silica gel, elution with n-hexane/DCM	GC/MS/MS	Recoveries (88 – 103%)	Tombesi *et al* 2017
Soxhlet (Acetone/hexane)	Silica column fractionation, elution with n-hexane/DCM	GC/MS		Li *et al* 2017
Soxhlet	Alumina glass column, elution with n-hexane/DCM	GC/ECD confirmed by GC/MS	Recoveries 84 – 91%), LOD (0,09 ng.g^{-1})	Rizzi *et al* 2017
Vortex (DCM/Hexane), ultrasonic agitation	Dispersive SPE, after centrifugation, solvent exchanged to isooctane	GC/MSD	Recoveries 72 – 117%), LOQ (0,2 – 10 ng.g^{-1})	Su *et al* 2017

HRGC – HRMS = high resolution gas chromatography - high resolution mass spectrometry, SPE = solid phase extraction, DCM = dichloromethane, GC/MS = gaz chromatography/mass spectrophotometry, GC/MSD = gaz chromatography/mass selective detector, GC/ECD = gaz chromatography/electron capture detector, GC/FID = gaz chromatography/flame ionization detector. LOQ/LOD = limit of quantification/limit of detection. GC/EI/MS = gaz chromatography/electron ionization/mass spectrometry

1.3. Organochlorine Pesticides (OCs)

1.3.1. Presentation

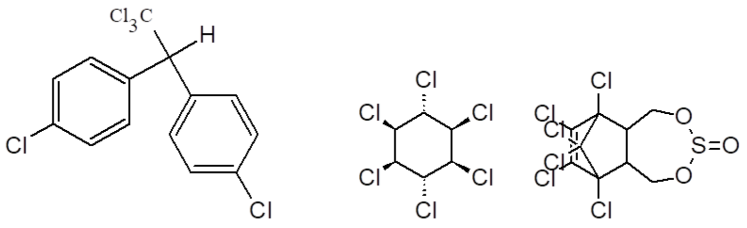
Pesticides are any substances or mixture of substances intended for preventing, destroying or controlling any pest including vectors of human or animal diseases, unwanted species of plants or animals causing harm during or otherwise interfering with the production processing, storage, or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pest in or on their bodies (FAO 1989; UNEP 1990; EPA 2009). The word pesticides may refer to insecticides, herbicides, fungicides or other pest control formulations. Representative compounds in this group include DDT, methoxychlore, dieldrin, chlordane, toxaphene, mirex, kepone, lindane, and benzene hexachloride. As neurotoxicants, many organochlorine pesticides were banned in the world, although a few are still registered for use in several countries (EPA 2009).

Pesticides are inherently toxic and often associated with adverse health effects in non-target organisms. Organochlorine pesticides are a large class of multipurpose chlorinated hydrocarbon chemicals. They break down slowly in the environment and accumulate in the fatty tissues of animals. Therefore, they stay in the environment and food web long after being applied. Many organochlorine pesticides are endocrine disrupting chemicals, meaning they have subtle toxic effects on the body's hormonal systems. Endocrine disrupting chemicals often mimic the body's natural hormones, disrupting normal functions and contributing to adverse health effects (Lemaire *et al* 2004).

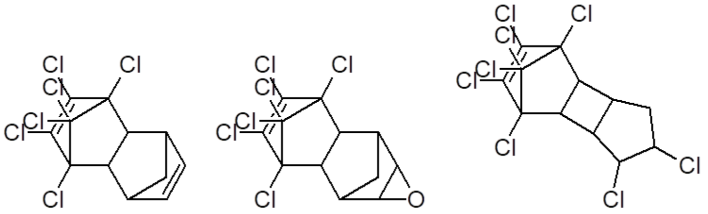
Numerous studies have linked organochlorine pesticides exposures with cancers and other health effects such as the behavioral alteration, reproductive effects and thyroid disruption. Exposure to DDT has been linked to pancreatic cancer and non-Hodgkin's. Hence, The Stockholm Convention on Persistent Organic Pollutants, a UN treaty, has established global bans on several organochlorine pesticides including DDT, hexachlorobenzene, pentachlorobenzene, chlordane, dieldrin, endrin, heptachlore, mirex, toxaphene, hexachlorocyclohexane (α-HCH, β-HCH, and λ-HCH), lindane and chlordecone. The European Union (EU) recently proposed that endosulfan be included under provisions of the Stockholm Convention as well. Although the US banned the use of lindane for agricultural uses, the Food and Drug Administration still allows use of lindane in pharmaceutical products for the treatment of head lice and scabies.

Additionally, these compounds were also grouped in the list of priority substances to be under control that was initially integrated in the water frame directive (WFD) by Decision n° 2455/2001/EC (EC 2001). From the total of 33 priority substances of the list, 11 were classified as "priority hazardous substances" (EC 2001). The list also includes 8 other substances that were already regulated at Union level (EC, 2008c). The EQSs for those substances were established by Directive 2008/105/EC (EC, 2008c). In 2013, Directive 2013/39/EU (EC 2013) amended the WFD and Directive 2008/105/EC (EC, 2008c) as regards priority substances in the field of water policy. New substances were included in the list of priority substances making a total of 45 substances or group of substances that will be under strictly surveillance in the next decades. Among these substances or groups of substances, 27 have been used as pesticides.

Pesticides can be classified based on their chemical compositions, their mode of action and the targeted pest species. However, the one we are interested on our work are according to the chemical composition. This classification is divided into four main group namely; organochlorines, organophosphorous, carbamates and pyrethrin and pyrethroids. Organochlorine pesticides are organic compound with five or more chlorine atoms. These are the first synthetic organic pesticides to be used in agriculture and in public health. Most of them were widely used as insecticides for the control of a wide range of insects, and they have a long-term residual effect in the environment since they are resistant to most chemical and microbial degradations. Organochlorine insecticides act as nervous system disruptors leading to convulsions and paralysis of the insect and it eventual death. Some of the commonly used representative example of organochlorine pesticides are DDT, lindane, endosulfan, aldrin, dieldrin and chlordane and their structures are presented here under (Figure 1.10). IUPAC name for DDT are1,1'-(2,2,2-Trichloroethane-1,1-diyl)bis(4-chlorobenzene, respectively.



p,p- DDT lindane Endosulfan



aldrin dieldrin chlordane

Figure 1.10. Chemical Structure of several Organochlorine Pesticides

DDT = Dichlorodiphenyltrichloroethane

Organophosphorous insecticides on the other hand contain a phosphate group as their basic structural framework as defined by Schrader’s formula:

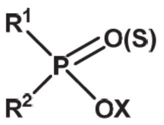
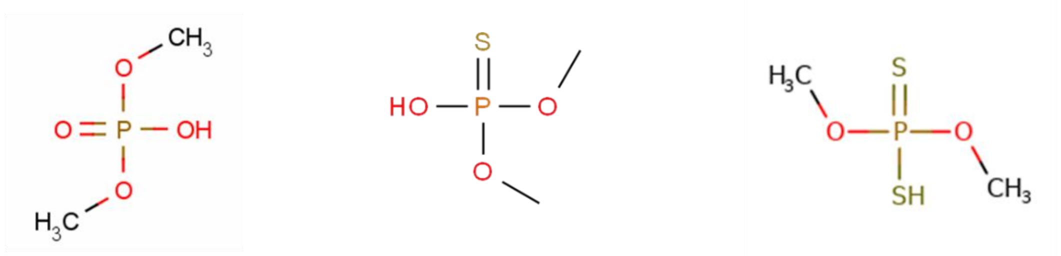
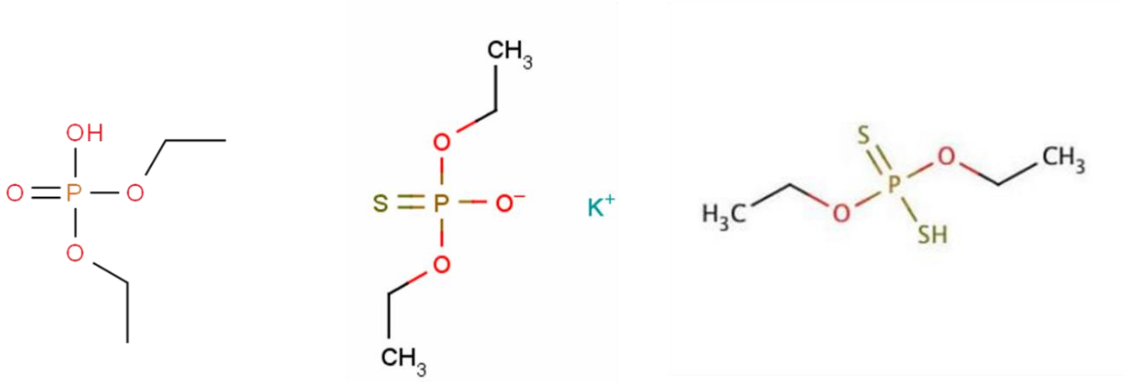


Figure 1.11. Basic Structural Framework of Organophophorous (Schrader’s Formula)

Where, R1 and R2 are usually methyl or ethyl groups, the O and OX group can be replaced with S in some compounds, whereas the X group can take a wide diversity of forms. Organophosphates (also known as phosphate esters) are a class of organophosphorus compounds with the general structure shown in Figure 1.11. They can be considered as esters of phosphoric acid. Such most functional groups organophosphates occur in a diverse range of forms, with important examples like insecticides, herbicides, and nerve agents. 6 examples of group-specific metabolite of organophosphate pesticides as described in Figure 1.12. Organophophorous inseticides are generally more toxic to vertebrate and invertebrates as cholinesterase inhibitors leading to a permanent overlay of acetylcholine neurotransmitter across a synapse. Some of widely used organophosphorous insecticides include parathion, malathion, diaznon and glyphosate.



Dimethyl Phosphate (DMP) **Dimethyl Tiophosphate (DTMP)** **Dimethyl Ditiophosphate (DMDTP)**



Diethyl Phosphate (DEP) **Diethyl Tiophosphate (DETP)** **Diethyl Ditiophosphate (DEDTP)**

Figure 1.12. Group-specific metabolites of the organophosphate pesticides

1.3.2. Physical and chemical properties of Organochlorine Pesticides

Molecular weight and form

The molecular weights of a pesticides is an inherent property that distinguish one pesticides from the other except for stereoisomeric pesticides which share similar molecular weight differing only on the group spatial orientations at given chiral centers. The common gas-phase pesicides for example have a molecular weight of about 103 or less. However, it becomes very difficult to predict the state and form of complex molecules with molecular weight that are substantially greater than 500.

Vapor pressure

For pesticides, the easy with which a pesticide can volatilize may be considered advantageous with respect to a particular mode of action on one hand, but it can be of negative influence on the other hand. For example, a pesticide with a fumigant mode of action can have a useful penetrative power and thus it is advantageous to have higher vapor pressure. However, a high vapor pressure can cause vapor drift and environmental pollution. Pesticides with high vapor pressure need to be handled in such a way so that the vapors do not escape into the atmosphere. A pesticide with low vapor pressure does not move into air, so there is a potential to accumulate in water if it is water soluble. If it is not water soluble, the pesticides may accumulate in soil or biota. They usually preferred SI-unit for vapor pressure is mille Pascal (Mpa = g.m^{-1}.$^{-2}$ or 0,001 N.M^{-2})

Solubility

Measurement of solubility are influenced by temperature, pH, polarity of the substance, hydrogen bonding, molecular size and the method used. The significance in environment fate of solubility of pesticides is that, a pesticide which is very soluble in water will tend not to accumulate in soil or biota because of its strong polar nature. This suggests that it will degrade via hydrlysis which is favored reaction in water.

Octanol/Water partition coefficient K_{ow} (Log K_{ow})

Kow is considered to be a good indicator of bioaccumulation of pesticides in organisms and food chains. Pesticides with a positive correlation to Log K_{ow} are more likely to have bioaccumulation effects to organisms and food chains. The parameter is also a good indicator of systemic mode of action of a pesticide. Pesticides with low K_{ow} values (generally ≤ 2) indicate the likely systemic translocation of such pesticides or their metabolites in the plants transvascular system. Kow values are generally influenced by the polarity of the pesticide and the general physical factors. Polar pesticides tend to be more soluble in water and hence low values of K_{ow}. For the general physical factors, Kow will increase when the following physical properties increase ; molecular surface area, molar volume, molecular weight, and density (Mallhot and Peters 1988).

Henry's Law Constant H'

This physical parameter measures the concentration of chemical in air over its concentration in water. It expresses the tendency of a material to volatilize from aqueous solution to air. The environmental significance of Henry's low constant is that, a pesticide with a high HLC value will volatilize from water into air and distribute over a large area. Conversely, a pesticide with a low HLC value tend to persist in water and may be adsorbed into soil and sediment.

Chemical properties of Pesticides

Following the release of pesticides in the environment, they undergo a complex series of interdependent processes that are collectively called chemodynamics of pesticides. These processes essentially determined by its inherent physico-chemical properties and partly by environmental parameters such as pH, temperature, moisture, precipitation, salinity, light intensity and topography. The major chemodynamic processes that determine the pesticides persistence, distribution and their ultimate fate in the environment include transportation, retention, degradation and biota uptake. Among all these chemodynamic processes, degradation is of much relevance with regard to this section as it entails the chemical transformations of pesticides in the environment, hence chemical properties of pesticides.

Degradation of pesticides is the breakdown or chemical transformation of pesticide molecules into others form that not necessarily simpler and less toxic compared to the parent molecule. In some cases the degradation products are also toxic and have some pesticidal effects as well. A good example of this is the degradation of DDT to DDD, which is itself a pesticide. The rate of degradation of pesticides is usually measured in terms of half-life ($t_{1/2}$), which is the time required for the depletion of half (or 50%) of the amount of pesticide present initially that is 2 – 15 years in the soils depending on soil acidity and temperature (ATSDR, 2002) . The degradation processes that bring about pesticides transformation can be categorized into two major groups ; chemical degradation and biological degradation. Chemical degradation generally occurs in water or atmosphere and it follows one of four reactions namely ; oxidation, reduction, hydrolysis and photolysis. Biological degradation generally occurs in soil and in living organisms and it utilizes one of four reaction ; oxidation, reduction, hydrolysis and conjugation. The type of the reaction in which a pesticide undergoes is largely determined by the pesticide inherent phyco-chemical properties and the environmental compartment (water, soil, air biota) in which it is hosted.

The bioconcentration factors, with reference to the levels of organochlorine pesticides residues in the river water samples as reported by Ibigbami *et al* 2015 in *Chrysichthys nigrodigitatus*, ranged from 0.84-12.8 while ranged from 0.22–9.86 for *Oreochromis niloticus* (Table1.9). The result revealed evidence of bioaccumulation of OCPs in the fish samples. α-BHC, β-BHC, lindane, endosulfan 1 and endosulfan sulphate were more persistent in *Chrysichthys nigrodigitatus* than the other OCPs. Dieldrin showed no evidence of bioaccumulation in *Chrysichthys nigrodigitatus*. In Oreochromis niloticus α-BHC, β-BHC, lindane and heptachlor were significantly accumulated (Ibigbami *et al* 2015). The bioconcentration factors of greater than one in most cases evidently indicated that the OCPs were highly bioaccumulated and biomagnified in the fish. Additionally, that Dieldrin and endosulfan II were not accumulated in *Oreochromis niloticus* fish samples as shown in Table 1.9 Lindane with the highest mean bioconcentration factor was the most bioaccumulated and biomagnified in *Chrysichthys nigrodigitatus* whilst endosulfan II was the least in *Oreochromis niloticus*. Levels of these pesticides residues in fish vary with species due to differences in biology (trophic level, habitat and reproductive season), exposure, detoxification capacity and ecology (Ibigbami *et al* 2015).

Table 1.9. Bioconcentration factor (BCF) of OC pesticides residues in *Chrysichthys nigrodigitatus* (CN) and *Oreochromis niloticus* (ON) in relation to water concentration (Ibigbami *et al.* 2015).

OCs	**CN**	**ON**
α-BHC	12.6	9.86
β-BHC	5.66	5.10
Lindane	12.8	6.92
λ-BHC	4.75	7.31
Chlorothalonil	4.09	1.39
Heptachlor	3.62	5.56
Aldrin	2.40	2.39
Heptachlor epoxide	2.70	3.23
Endosulfan I	7.91	1.96
Dieldrin	-	0.93
Endrin	4.45	1.33
Endosulfan II	2.20	0.22
p,p' – DDD	4.86	1.85
Endosulfan sulphate	9.48	2.15
p,p' - DDT	0.84	3.97

1.3.3. Use

In spite of the degree of toxicity, pesticides are still used in many fields. The application of these chemicals are aimed at controlling undesirable organisms occurs throughout the world at an annual rate of 2.5 billion kg of active ingredients. The main market is agriculture and related industries such as : forestry, horticulture, producing food and commodities. The pesticides are also used in health programs and for construction preservation.

Food preservation

The use of pesticides leads to maximization of the food and commodity production by helping to prevent losses during growth, harvest, transport, storage and distribution. Statistics claim a 30 - 35% of the world production is lost each year even with the application of modern agriculture techniques. Crop losses would be doubled if the pesticides were eliminated. Due to pesticides, the yields are improved and the crop is protected, the protection is also realized during food storage.

Disease Control and Public Health

Pests may also affect health also. A wide range of pests act as carriers in the transmission of diseases to animals or humans. Species like lice, mites and mosquitoes act as vectors for bacterial, protozoal or viral diseases. Infections can be generated by bites or stings and sometimes also by mechanical effects (insect feet). Among the diseases spread by pests there are: malarialeotospirosis, salmonellosis, plague, typhus and hemorrhagic fevers. For eradicating these diseases the destruction of the vector-pests is absolutely necessary. Pesticides are a solution for the elimination of these pests.

Preservation and Maintenance

An important field of pesticide application is wood preservation. Most of the buildings have wood in their composition. Repair and replacement of it involve high costs. Thus, preservation using pesticides is usually applied. Special bacteria destroy also cement. For protection pesticides may be of help. Parks, sports grounds like: public golf, football or tennis courses, botanical, and zoological gardens and other entertainment facilities are preserved by regularly using pesticides.

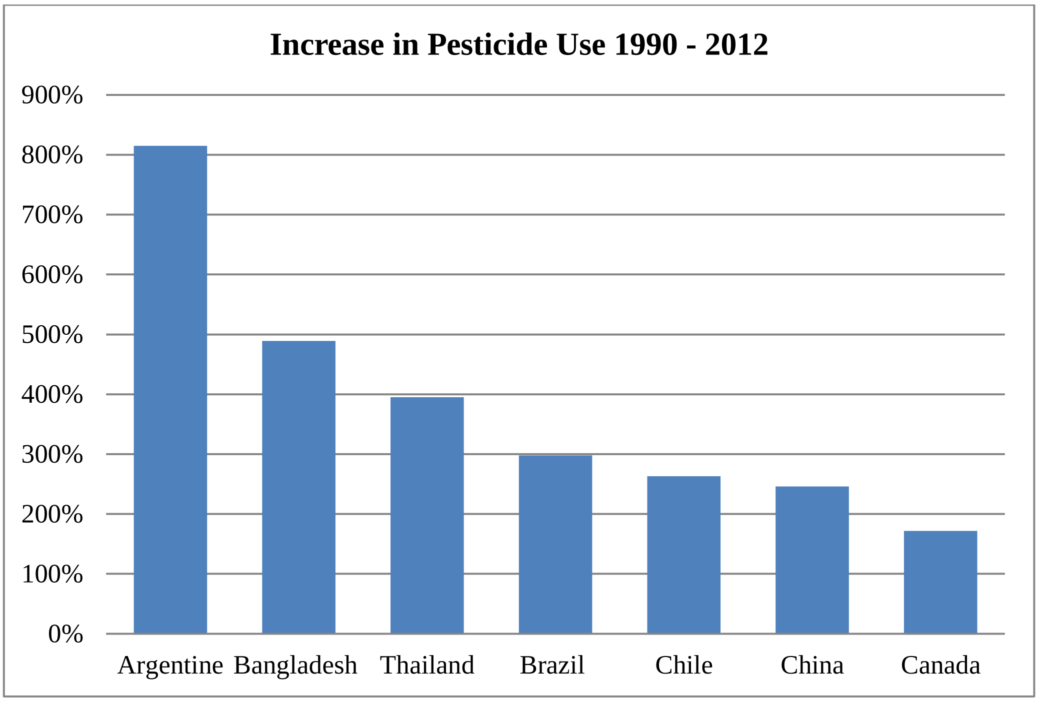


Figure 1.13. Pesticides uses (Pretty and Bharucha, *Insect*, 2015).

Concerning the use of pesticides through some of the interests mentioned above, some countries as illustrated in the graph above show a significant increase from 2007 to 2012. Countries with the highest use of pesticides are Argentina followed by Bangladesh and Thailand respectively which increased by 815% 459% and 395% (Figure 1.13). Whereas, the country with the least use of pesticides is Canada. Through this graph, it is also clearly seen that overall, there is an increasing use of pesticides in various interests in some developed and developing countries with the agricultural industry as a mainstay sector.

It can be concluded that while some laws and regulations have been established considering their hazard effects, these chemical compounds are continuing to be found in the environment as a result of the remnants of their use in various sectors. Therefore, research on the concentration levels of these pesticides in the environment is very important to be carried out, in order to provide the complete information to facilitate the monitoring of the effects or disturbances of these compounds both on the environment and the health of human beings.

1.3.4. Sources, fate and transport of pesticides

Once pesticides are applied to the areas such as homes, offices, lawns, gardens, fields, and water sources they become mobile in the environment. Several factors affect how a pesticide will move in the environment once it is introduced. Some of the factors that affect pesticide movement are how much these compounds are applied since the excess pesticides that do not reach their target organisms are free to move in the environment in other way when they are used beyond recommended quantities. Then, how and where these chemicals are applied; for instance, a liquid pesticide applied from a large sprayer over a farm field will have different considerations, in terms of transport and fate, than solid pellets of pesticide applied around the foundation of a house. Moreover, when these substances are applied, this means that they are based upon conditions such as weather or season. For example, a liquid pesticide sprayed from an aerosol will fall to the ground or move with the air. The amount that moves with the air will depend upon wind conditions. Seasons can affect pesticide transport, as well. Some of the factors that are seasonal are temperature (both inside and outside), humidity, rain, and snowmelt (Li *et al* 2014; Duodu *et al* 2017; Škrbić *et al* 2017; Liu *et al* 2018)

It is important to remember that pesticides have the potential to move in many environmental mediums and that their movement is three-dimensional. Pesticides can build up anywhere that soil, water, air, and the tissues of organisms such as birds, fish, and humans can transport them (Nakata *et al* 2005; Zhou *et al* 2013; Wang *et al* 2018).

Pesticide Transport in Air

Pesticides, regardless of the medium that they are applied in, all have the potential to be transported by air. Airborne pesticides can move very long distances and can occur in several ways. They can be carried in the wind during application. They can be carried on small particulates such as soil or on larger objects like leaves that are caught up by wind, and they can volatilize off of any surface that they are applied to. Deposition is what occurs when the wind carrying a pesticide slows down enough that its velocity can no longer hold it in the air, and it falls on whatever is beneath it. This is called “dry deposition.” Very small particulates or molecules of pesticide may remain in the atmosphere even when the air is relatively still. These pesticides may be removed from the atmosphere when it rains and the droplets catch them on their way down. This process is called “wet deposition.” (Takazawa *et al* 2016; Chen *et al* 2017; Holt *et al* 2017; Gevao *et al* 2018).

Pesticide Transport in Water

Water transport of pesticides can occur through wet deposition, run-off from surfaces, infiltration of water through the ground, ditches, storm sewers, tile lines, drains, rivers (Papadakis *et al* 2018 ; Wang *et al* 2018a; 2018b), and open water currents (Lin *et al* 2012; Pućko *et al* 2017; Wu *et al* 2017; Liu *et al* 2018; Placencia and Contreras 2018). Water can behave much like air in terms of transporting pesticides. Water that is moving at a high velocity can carry heavier pesticides, or particles that pesticides may be attached to, then water that is moving slowly. Faster moving water also has the potential to move pesticides farther. Pesticides in open water systems may float on the water, diffuse into the water, or deposit onto the sediments at the bottom of the water body. Pesticides that move from the ground surface through the soil may reach shallow ground water or deeper aquifers.

Pesticide Transport in Soils

Once a pesticide is in the soil it will most likely follow one of three pathways (Chakraborty *et al* 2015; Sánchez-Osorio *et al* 2017). It will move through the soil with water, attach to soil particles, or be metabolized by organisms in the soil. Soil texture (percent sand, silt, and clay) and structure plays a large role in the transport processes of pesticides. Soils that are very sandy will allow water to move through them quickly, do not attach easily to pesticides, and generally do not contain a large population of soil organisms relative to other soil types. Soils that are high in clays and organic matter will slow the movement of water, attach easily to many pesticides, and generally have a higher diversity and population of soil organisms that can metabolize the pesticide (Cheng *et al* 2016; Chen *et al* 2017).

Pesticide Transport in Organisms

There are pesticides that can accumulate in the tissues of organisms. This process is called bioaccumulation. Generally, bioaccumulation results in higher concentrations of a chemical as one goes further up the food chain. Pesticides that bioaccumulate in organisms are often very persistant in the environment. They do not "break down" easily and retain their form even when ingested and stored in the body. Most pesticides that have these characteristics have been banned from use in the United States of America, though such pesticides that were used historically are still present in the environment.

1.3.5. The Alteration in the Environment

Biotic and abiotic are the essential factors which play the key roles of these substances existent in the environment. The rate at which the different pesticides are biodegraded varies widely. Some pesticides such as DDT and dieldrin were proven to be recalcitrant (Zaffar *et al* 2016). Consequently, they remain in the environment for a long time and accumulate into food chains for decades after their application to the agriculture industrial (Junqué *et al* 2018; Yu *et al* 2018; Zhou *et al* 2018).

The majority of the studies including the biodegradation of organochlorine pesticides were carried out in pure cultures (Abraham *et al* 2014; Briceno *et al* 2016; Kumar *et al* 2018). The culture was usually isolated from a soil sample, generally contaminated with organochlorine pesticides. The strains were characterized and tested with different concentrations of the pesticide studied. DDT-metabolising microbes have been isolated from a range of habitats, including, soil, sewage, activated sludge, and marine and freshwater sediments (Pesce *et al* 2013; Fang *et al* 2014; Garcia-Cruz *et al* 2018; Shabbir *et al* 2018; Wang *et al* 2018). The degradation of organochlorine pesticides by pure cultures has been proven to occur in situ.

There are various micro-organisms involved in the degradation of organochlorine pesticides such as : *Alcaligenes sp, Ochrobactrum sp, Sphingobacterium sp, Enterobacter ludwigii, Pseudomonas moraviensis, Serratia marcescens, Klebsiella pneumonia* (Abraham *et al* 2014). On the other hand, some microbes such as Aspergillus, Chlorella, and Arthrobacter, are capable of coupling a variety of physical and biochemical mechanisms for the degradation of organophosphate pesticides, including adsorption, hydrolysis of P–O alkyl and aryl bonds, photodegradation, and enzymatic mineralization. Enzymes, such as esterase, diisopropyl fluorophosphatase, phosphotriesterase, somanase, parathion hydrolase, and paraoxonase, have been isolated from microbes to study and understand the catabolic pathways involved in the biotransformation of these xenobiotic compounds (Kumar *et al* 2018).

Nawab *et al* (2003) were able to prove the breakdown of dieldrin γ-HCH in the soil by a Pseudomonas sp. The bacteria strain was isolated from agricultural soil sample. Whereas white rot fungi has the capacity to degrade a wide spectrum of recalcitrant organic pollutants including dieldrin and aldrin over 90% after 28 d incubation in a low nitrogen medium. These fungi involved Phlebia acanthocystis, Phlebia brevispora, and Phlebia aurea (Xiao *et al* 2011).

In order to assess several factors that affect the capacity of biodegradation of DDT by a *Sphingobacterium sp*. Fang *et al* (2010), studied the biodegradation at the different temperatures, pH, concentrations of DDT and with an additional source of carbon. Yields of the experience showed that the degradation rates were proportional to the concentrations of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE ranging from 1 to 50 mg.l^{-1}. The ability of Sphingobacterium sp. to degrade DDTs was somewhat inhibited by DDTs at the level as high as 50 mg.l^{-1}. Accordingly, this may be due to the fact that DDTs at high concentration are toxic to Sphingobacterium sp. and inhibit degradation. The experiment was also tested for different pH, it was tested for pH 5, 7 and 9. The results indicated that a neutral condition is favorable for the degradation of DDT by Sphingobacterium sp., whereas higher or lower pH inhibits degradation. The influence of the temperature on the biodegradation was investigated by performing the experiments at temperatures of 20, 30 and 40°C. The results indicated that the optimum temperature for the biodegradation of DDTs by a Sphingobacterium sp. in pure culture was at 30°C. Ultimately, the biodegradation was available with an additional carbon source and results showed that the degradation half-lives of DDTs in the presence of glucose, yeast extract, sucrose, and fructose were significantly shorter than those in the treatment without an additional carbon source; and that the presence of glucose generates the fastest degradation of DDTs (Fang *et al* 2010).

1.3.6. Toxicity

Most of the pesticides are toxic for humans and domestic animals. They lead to allergy, cancer or even death. In order to avoid intoxications application doses are limited and specific protection measures are taken. The toxic effect may appear instantly or after a while. In the former case the symptoms are: headaches, nausea, tiredness, vomit, difficulty in breathing (Stallones and Beseler 2002; Dasgupta *et al* 2007) and some neuropsychological impairment (Reidy *et al* 1992). In the later case the effects appear in time leading to cancer or children cytogenetic damages (George and Shukla

2011; Attaullah *et al* 2017; Ruiz-Guzmán *et al* 2017; Valcke *et al* 2017). In such case the connection with pesticide-intoxication is difficult to be established due to the period of time in between (latency period). Cancer manifests itself after almost 10 years and mutations (genes defects) or child malformations go to the next generation.

Moreover, food consumption with large amounts (grams) of DDT over a short time would most likely affect the nervous system. People who swallowed large amounts of DDT became excitable and had tremors and seizures. They also experienced sweating, headache, nausea, vomiting, and dizziness. These effects on the nervous system went away once exposure stopped. The same type of effects would be expected by breathing DDT particles in the air or by contact of the skin with high amounts of DDT (ATSDR 2002)

No effects have been reported in adults given small daily doses of DDT by capsule for 18 months (up to 35 mg every day). People exposed for a long time to small amounts of DDT (less than 20 mg per day), such as people who worked in factories where DDT was made, had some minor changes in the levels of liver enzymes in the blood. A study in humans showed that increasing concentrations of p,p'-DDE in human breast milk were associated with reductions in the duration of lactation. An additional study in humans found that as the DDE levels in the blood of pregnant women increased, the chances of having a pre-term baby also increased. It should be mentioned, however, that the levels of DDE in the blood at which this was noticed were higher than those currently found in women from the general population in the United States, but not higher than those that may be found in women in countries where DDT is still being used (ATSDR, 2002)

Furthermore, the toxicity of each pesticide has to be known in order to prevent accidents. Usually it is expressed by the lethal dose LD_{50}. It represents the quantity of pure substance ($mg.kg^{-1}$ body weight), taken orally or by contact, causing the death to 50% of the exposed animals (in most cases rats) (Gaines and Linder 1986; Hamadache *et al* 2016) in a definite period of time. Higher toxicity means lower values of LD_{50}. Additionally, these compounds can reduce the adult fertility of rats as well (Elbetieha *et al* 2001).

To assess the potential risk of the pesticides on consumers of the aquatic resources, the guidelines for potential risk assessment was evaluated. (Ibigbami *et al* 2015) showed the estimated dose values and hazard indices of OCs in contaminated *Chrysichthys nigrodigitatus* and *Oreochromis niloticus* fish samples from the study river. The hazard indices for children (1-11 years) and adults were estimated as ratios between estimated daily intakes and available daily intake.

The results showed that the 15 analysed OCs from the samples pose no threat to the consumer's health if consumed except endosulfan sulphate in *Chrysichthys nigrodigitatus*. Comparing the estimated available daily intake of each pesticide for the children and adult from the study area with reference dose of WHO/FAO ADI, all the 15 analysed pesticides were significantly lower than available daily intake as stipulated by FAO. An aggregate daily exposure to a pesticide residue at or below the reference dose (Rfd) is generally considered acceptable by the USEPA. which are considered to be safe levels of exposure over lifetime. Endosulfan sulphate in *Chrysichthys nigrodigitatus* could pose potential health risk to children while the hazard index of endosulfan sulphate in *Chrysichthys nigrodigitatus* could also be dangerous to adult if consumed over time because the hazard index (0.048) of *Chrysichthys nigrodigitatus* in adult was close to the reference dose ($0.05\ \mu g.kg^{-1}.day^{-1}$) of endosulfan sulphate whilst the other determined pesticides in the fish pose no hazard to the health of the people (Ibigbami *et al* 2015).

Another possible effect of pesticide is the disturbance of the immunity system of the living organisms (James and Xu 2012; Martyniuk *et al* 2016; Cowie *et al* 2017; Ghazy *et al* 2017). There is evidence of immuno-toxic effects of organo-phophorus compounds on animals and humans. These pesticides allow cancer development due to immune suppressant activity (Attaullah *et al* 2017; Rodríguez *et al* 2017; Valcke *et al* 2017). The allergic reactions are definite proof for the disturbance of the immune system. A number of experimental studies revealed also endocrine effects (Ewence *et al* 2015; Combarnous 2017; Song *et al* 2017; Westlund and Yargeau 2017), because some of the pesticides may mimic hormones. Some possible effects on human health such as cancer (breast, prostate, brain); endometrioses; abnormal sexual development; damages of the functions of hypothalamus and thyroid; risk of Parkinson's disease (Tian *et al* 2012; Kalliora *et al* 2018; Bapayeva *et al* 2016).

Moreover, pesticides have ecological impact not only to human being but also toward natural ecosystem. The environmental toxicity, known as ecotoxicology experienced better attention looking for impact of pesticides on biotic and abiotic elements (Montuori *et al* 2016; Wee *et al* 2017; Kuan *et al* 2018; Moro *et al* 2018; Weber *et al* 2018).

1.3.7. Occurrence of OCs pesticides in Sediments throughout the World

We have reviewed 32 articles on the occurrence of ∑OCs concentrations in sediments during 1995 to 2017 as summarized in the Table 1.10 below. The first decade, the concentration levels of these chemicals in surface sediments ranged from <0.005 to 72 ng.g^{-1}. The highest concentration was found around urban and industries area at the Lake of Simbirizzi, Italy as the punctual pollution (Kaljzic *et al* 1998). While the lowest one was recorded at the Great Barrier Reef, Queensland, Australia where connencted with agricultural activities (Cavanagh *et al* 1999). Additionally, at the remmote area of Green Land, these compounds were detected as of 11 to 26 ng.g^{-1} dw (Cleemann *et al* 2000). This suggested that OCs are found not only at the area where activities of agriculture are occurring but also at the location where are not connected with Pesticides uses, even at the remote area (Cleemann *et al* 2010)

Since 2009 to present, the concentration levels of OCs ranged from 0.0019 ng.g^{-1} to 168524 ng.g^{-1}) The most elevated concentration of these compounds was recorded at the agricultural area at Chao River sediments of China (Yu *et al* 2014). Whereas the lowest one was found at the Red Sea Coast sediments of Egypt (Ragab *et al* 2016) where was linked with petroleum, agriculture, fishery and shipping traffic. This imply that OCs are still using in several application despite of the restriction since 1970, either in industries or in agricultural activities particularly in Asia and South America.

Table 1.10. Occurrence of OCPs in Sediments throughout the World (1995 to 2017)

Activities in land	Concentrations	Locations	References
Unpolluted area	∑OCs (0.01 – 3.40 ng.g^{-1})	Canadian Arctic Lake	Muir *et al* (1995)
Industries and agriculture activities	∑OCs (0.10 – 25 ng.g^{-1})	West Coast of India	Sarkar *et al* (1997)
Urban and industry activities	∑OCs (0.02 – 72 ng.g^{-1})	Lake Simbirizzi, Italy	Kalajzic *et al* (1998)
Connected to agricultural activities	∑OCs (<0.005 – 46 ng.g^{-1})	Great Barrier Reef, Queensland, Australia	Cavanagh *et al* (1999)
Remote area	∑OCs(11 – 26 ng.g^{-1})	Greenland	Cleemann *et al* (2000)
Industrial and agricultural activities	∑OCs (<MDL – 2.1 ng.g^{-1})	Winnipeg Lake, Canada	Rawn *et al* (2000)

Petroleum refiners, agriculture area	∑OCs (<0.1 – 11.9 ng.g^{-1})	Coastal area of Singapore	Wurl and Obbard (2005)
Municipal and Industrial sewage	∑OCs (1.63 – 22.7 ng.g^{-1})	Quanzhou Bay, Southeast China	Gong *et al* (2007)
Industrial and wastewater discharge	∑OCs (2.1 – 21.3 ng.g^{-1})	Bohai Sea, China	Tan *et al* (2009)
Industries, agricultures, effluents discharges	∑OCs (0.08 – 26 ng.g^{-1})	Coastal area, Portugal	Carvalho *et al* (2009)
Agricultural area	∑OCs (0.16 – 90 ng.g^{-1})	Laizhou Bay, North China	Zhong *et al* (2011)
Industries, high populated and agriculture activities	∑OCs (nd – 15.96 ng.g^{-1})	Lake of Victoria, Uganda	Wasswa *et al* (2011)
Agricultural area	∑DDTs (0.2 – 2.30 ng.g^{-1})	North Eastern France	Thomas *et al* (2012)
Connected to agricultural area	∑OCs (0.14 – 5.67 ng.g^{-1})	Coastal East China Sea	Lin *et al* (2012)
Urban, agriculture, shipping, industry	∑OCs (<LOQ – 0.74 ng.g^{-1})	Guaratuba Bay, SW Atlantic	Combi *et al* (2013)
Untreated municipal effluents, connected to sewage and agriculture	∑OCs (nd - 249 ng.g^{-1})	Mediterranean Sea, Egypt	Barakat *et al* (2013)
Agricultural area12	∑OCs (4.68 – 42.95 ng.g^{-1})	Hong Hu Lake, China	Yuan *et al* (2013)
Connected to agricultural area	∑OCs (0.06 – 5.8 ng.g^{-1})	Hangzhou, China	Wu *et al* (2013)
Agricultural area1	∑OCs (0.81 – 168524 ng.g^{-1}	Chao River, China	Yu *et al* (2014)
Agricultural soil, farm land, vegetable production	∑OCs (144 ng.g^{-1})	Manufacturing region, China	Zhu *et al* (2014)
Industrial, agricultural, urban effluents, land-base activities	∑OCs (0.09 – 13.61 ng.g^{-1})	Egyptian, Mediterranean Sea	Aly Salem *et al* (2014)
Fishing and industy	∑OCs (0.02 – 0.32 ng.g^{-1})	Gulf of Batabano, Cuba	Alonso – Hernandez *et al* (2015)
Industrial and domestic discharged	HCHs (0.13 – 4.77 ng.g^{-1}) DDTs (0.11 – 3.54 ng.g^{-1})	Liaohe Estuary, China	Li *et al* (2016)
Urban, Largest agriculture and high populated	∑OCs (0.66 – 10.2 ng.g^{-1})	Tiber River and Estuary, Italy	Montuori *et al* (2016)
Petroleum, agriculture, fishing, shipping traffic	∑OCs (0.0019 – 0.106 ng.g^{-1})	Red Sea Coast, Egypt	Ragab *et al* (2016)
Fishery and harbor activities	∑OCs (2.19 – 16.9 ng.g^{-1})	Shantou Bay, China	Shi *et al* (2016)
Port activities	∑OCs (0.11 – 50.73 ng.g^{-1})	Mediterranean Sea, Egypt	Nemr and El Sadaawy (2016)
Connected to agricultural area and domestic and industrial effluents	∑OCs (1.48- 6.52 ng.g^{-1})	Eastern, Aegean Coast, Turkey	Muzyed *et al* (2017)
Industrial, high populated, wastewater discharged	∑OCs (16,3 – 96,9 ng.g^{-1})	Taihu Lake and it tributaries rivers, China	Zhao *et al* (2017)
Agricultural area	∑HCHs (0.034 – 8.0 ng.g^{-1}) ∑DDTs (nd - 268 ng.g^{-1})	North Mexico	Sanchez-Ozorio *et al* (2017)
Industry, agriculture and transportation	∑OCs (0.3 – 4.5 ng.g^{-1})	Plateau Lake, China	Yuan *et al* (2017)

DDD = Dichlorodiphenyldichloroethane, DDT = dichlorodiphenyltrichloroethane, DDE = dichlorodiphényldichloroéthylène, HCH = hexachlorocyclohexane, OCs = Organochlorines, MDL = Method detection limit, LOQ = Limit of quantification.

1.3.8. Review of analytical methods

The analytical methods and techniques that employed to assess and to measure OCs in the sediment matrices vary due to the complexity of the matrices and broad ranges of OCs pollutants found in the environment. In this work, we have reviewed 30 articles that have been published in the scientific journals throughout the world from 1995 to 2017 (Table 1.11). Various samples preparation techniques, such as mechanical shaker and microwave (Sarkar *et al* 1997; Alonso-Hernandez *et al* 2015; Muzyed *et al* 2017) and sonication (Montuori *et al* 2016) applied for the extraction of OCs with good recoveries from 70 to 88%. However, scientist tended to use soxhlet, the classical extractor to assess these compounds (Muir *et al* 1995; Cavanagh *et al* 1999; Cleemann *et al* 2000; Gong *et al* 2007; Tan *et al* 2009; Zhong *et al* 2011; Lin *et al* 2012; Combi *et al* 2013; Wu *et al* 2013; Aly Salem *et al* 2014; Yu *et al* 2014; Zhu *et al* 2014; Li *et al* 2016; Ragab *et al* 2016; Shi *et al* 2016; Rizzi *et al* 2017; Sanchez – Ozorio *et al* 2017) with a very good recoveries of 66 to 100%.

Concerning purification of these OCs, almost 80% of the publications used alumina silica glass column to cleanup and separate these pesticides from sediment matrices with more than 70% recoveries. Almost two decades, trace analysis determination for OCs has been dominated by GC/MS and GC/ECD. Despite the growing number of study reports using GC-ECD as the instrumental technique for detecting OCs compounds in the sediments, a GC/MS is still the instrument of choice for analyzing these OCs. Numerous studies (Wurl and Obbard 2005; Combi *et al* 2013; Li *et al* 2016; Yu *et al* 2016; Zhu *et al* 2016; Rizzi *et al* 2017; Ragab *et al* 2016) reported successfully development methods to identify OCs using GC/MS technique.

Table 1.11. Review of Analytical Method (1995 to 2017)

Extraction	Purification	Identification	Performance	References
Soxhlet (DCM)	Florisil column, elution with DCM/hexane	GC/ECD confirmed by GS/MS	Recoveries (70 - 100%), MDL (0.02 ng.g^{-1})	Muir *et al* (1995)
Shaker (hexane/acetone)	Silica gel column, elution with hexane	GC/ECD		Sarkar *et al* (1997)
Mechanical shaker (hexane/acetone)	Silica gel column, elution with hexane/diethyl ether	HRGS/ECD	Recoveries (99%),	Kalajzic *et al* (1998)
Soxhlet (DCM)	Silica alumina column, elution with hexane/DCM	GS/MS	Recoveries (70 - 110%), MDL (25 pg.g^{-1})	Cavanagh *et al* (1999)
Soxhlet	Silica alumina column	GC capillary column with different polarity	Recoveries (94%),	Cleemann *et al* (2000)
ASE (hexane/DCM)	Florisil column, elution with hexane/DCM	GC/ECD	Recoveries (66 - 74%),	Rawn *et al* (2000)
Microwave oven (acetone/hexane)	Silica gel column, elution with hexane/DCM	GC/MS	Recoveries (69 - 123%),	Wurl and Obbard (2005)
Soxhlet (DCM)	Alumina silica glass column, elution with DCM/hexane	GC/ECD	Recoveries (78 - 105%),	Gong *et al* (2007)
Soxhlet (hexane/ DCM)	Alumina silica gel column, elution with	GC/ECD	Recovery (83%)	Tan *et al* (2009)

	hexane/DCM			
Shaker (acetone/cyclohexane)	Gel permeation chromatography (GPC), elution with ethyl acetate/cyclohexane	GC/ECD	MDL (0.0153 ng.g^{-1})	Wasswa *et al* (2011)
Soxhlet (DCM), solvent exchanged to hexane	Alumina silica glass column, elution with DCM/hexane	GC/ECD	Recoveries (66 – 102%), MDL (0.001 – 0.018 ng.g^{-1})	Zhong *et al* (2011)
Soxhlet (DCM) solvent exchanged to hexane	Alumina silica gel column, elution with hexane/DCM	GC/ECD	Recoveries (81 – 103%), MDL (0.04 – 0.31 ng.g^{-1})	Lin *et al* (2012)
Cryogenic extraction (Acetone/hexane)	SPE C18 florisil	GC/ECD	LOD (0.03 ng.g^{-1})	Thomas *et al* (2012)
Soxhlet (DCM)	Alumina silica gel column, elution with hexane/DCM	GC/ECD	Recoveries (85%), MDL (0.01 – 0.05 ng.g^{-1})	Yuan *et al* (2013)
Soxhlet (DCM) solvent exchanged to hexane	Silica gel column, elution with hexane/DCM	GC/NIMS	Recoveries (81 – 102%), MDL (0.04 – 0.07 ng.g^{-1})	Wu *et al* (2013)
Soxhlet (DCM/ hexane	Alumina silica glass column, elution with DCM/hexane	GC/ECD confirmed with GC/MS	Recoveries (86 – 95%),	Combi *et al* (2013)
ASE (DCM)	Alumina silica glass column, elution with DCM/pentane	GC/ECD	Recoveries (91%), MDL (0.25 ng.g^{-1})	Barakat *et al* (2013)
Soxhlet (hexane/acetone)	Alumina silica gel column, elution with hexane/DCM	GC/MS	Recoveries (74 – 142%)	Zhu *et al* (2014)
Soxhlet	Glass column florisil, elution with hexane /DCM	GC/ECD	Recoveries (97 – 113%)	Aly Salem *et al* (2014)
Soxhlet (hexane/acetone)	Alumina silica gel column, elution with hexane/DCM	GC/MS		Yu *et al* (2014)
Microwave oven (methylene chloride/hexane)	Alumina silica glass column, elution with methylene chloride/hexane	HRGC-ECD	MDL (10 – 30 pg.g^{-1})	Alonso – Hernandez *et al* (2015)
Sonication	Alumina silica gel column, elution with hexane	GC/ECD	Recoveries (88%), LOD (0.008 – 0.09 ng.g^{-1})	Montuori *et al* (2016)
Soxhlet (hexane/acetone/DCM)	Alumina silica gel column, elution with hexane/DCM	GC/MS	Recoveries (82 – 103%)	Shi *et al* (2016)
Soxhlet (hexane/acetone)	Alumina silica gel column, elution with hexane/DCM	GC/MS		Li *et al* (2016)
Soxhlet (hexane/DCM)	Florisil glass column, elution with DCM/hexane	GC/MS	Recoveries (91 – 104%)	Ragab *et al* 2016
Pre-cleaned extraction thimble (hexane/DCM	Florisil glass column, elution with DCM/hexane	GC/ECD	Recoveries (93 – 107%),	Nemr and El Sadaawy 2016
ASE (hexane/methanol)	Alumina silica gel column, elution with hexane/DCM	GC/MS	Recoveries (81 – 107%), LOD (0.01– 1.02 ng.g^{-1})	Yuan *et al* (2017)
Soxhlet (DCM)	Alumina silica gel column, elution with	GC/ECD confirmed	Recoveries (74%), LOD (0.10 ng.g^{-1})	Rizzi *et al* (2017)

	DCM	with GC/MS		
ASE (DCM)	Alumina silica gel column, elution with DCM	HPLC-DAD-FLD	Recoveries (69 – 112%), IDL (0.01 – 2.81 ng.g^{-1})	Zhao *et al* (2017)
Soxhlet (DCM)	Alumina silica gel column, elution with hexane/DCM	GC/EI/MS	Recoveries (56 – 139%), IDL (0.002 – 0.014 ng.g^{-1})	Sanchez-Ozorio *et al* (2017)
Microwave digestion system (hexane/DCM)	Florisil glass column, elution with DCM/hexane		Recoveries (70 - 96%), MDL (0.10 – 0.57 pg.g^{-1})	Muzyed *et al* (2017)

DCM = dichloromethane, HPLC = high performance liquid chromatography, GC/MS = gaz chromatography/mass spectrophotometry, GC/MSD = gaz chromatography/mass selective detector, GC/FID = gaz chromatography/flame ionization detector. GC/ECD = gaz chromatography/electron capture detector, GC/EI/MS = gas chromatograph-electron impact-mass spectrometer, LOD = limit of detection, SPE = solid phase extraction, HPLC-DAD-FLD = high-performance liquid chromatography coupled to a diode array detector or fluorescence detector, HRGC/ECD = high resolution gas chromatography/electron capture detector, MDL : method detection limit.

1.4. Linear Alkylbenzenes (LABs)

1.4.1. Presentation

Linear alkylbenzene is a family of organic compounds with the formula $C_6H_5C_nH_{2n+1}$. Typically, n lies between 10 and 16, although generally supplied as a tighter cut, such as C_1 – C_{15}, C_1 – C_{13} and C_{10} – C_{13}, for detergent use. The C_nH_{2n+1} chain is unbranched. They are sometimes called LABs. Alkylbenzenes are the most widely used surfactant raw materials. There are two basic types of alkylbenzenes used in surfactant manufacturing: linear alkylbenzenes (LAB) and branched alkylbenzene (BAB). Both types of alkylbenzenes are homolog mixtures. Typical homolog representatives of LAB and BAB are depicted in Figures 1.14 and 1.15 respectively.

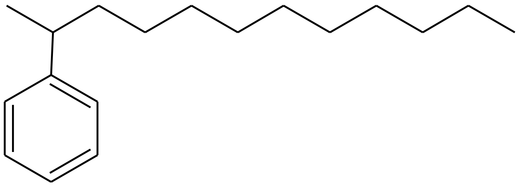


Figure 1.14. Simple linear alkylbenzene (2-phenyldodecane)

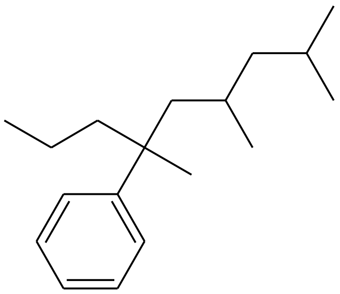


Figure 1.15. Structure of a branched alkylbenzene (4-phenyl-4, 6, 8-trimethylnonane)

As one of the problematic compound in the marine environment, it has been subjected to concern about their adverse effects not only to the environment but also human health. European Council Regulation (EC) 1488/94(10) proposed that these LABs should be extensively evaluated. The life-cycle analysis considered the emissions and resulting environmental and human exposures. Following the exposure assessment, the environmental risk characterization for each protection target in the aquatic, terrestrial and soil compartment was determined. For human health, the scenarios for occupational exposure, consumer exposure and human exposure indirectly via the environment have been examined and the possible risks identified.

The report concludes that there are no concerns for the environment or human health. There is no need for further testing or risk reduction measures beyond those currently practiced. LAB was therefore de-classified and was removed from Annex 1 in the 28th ATP (Directive 2001/59).

1.4.2. Physical and Chemical Properties of LABs

LABs present in the environment as a biodegradable product of LAS that are difficult to characterize and measure. They are generally analyzed by gas chromatography coupled with mass spectrometry or by high performance liquid chromatography coupled with UV or fluorometric detectors. The physical and chemical properties, as well-described in Table 1.3. such as their water solubility is low and their octanol/water partition coefficient (Log K_{ow}) is relatively high (7.5 – 9.12 at 25ºC). These properties provide them an important adsorption potential on particles suspended in air or in water, sediment and soil. These chemicals are stable but photosensitive as well (Petrović and Barceló, 2000). Calculated half-lives for various alkyl homologues are similar but ranged from 12 to 15 days (Holt and Bernstein, 1992). This is confirmed in time course samples which show half lives of 4.5 days for the 2-phenyl isomers and 20 days for the 6/7-phenyl isomers.

Table 1.12. Physical and Chemical Properties of LABs

Appearance	Clear, colorless liquid
Odor	Odor less
Solubility in water	Slightly soluble
Relative Density (H_2O = 1)	0.858 – 0.868 @ 15.5ºC
Boiling Point ºC	278 – 314ºC
Melting Point ºC	< -70ºC
Relative Vapor Density (Air = 1)	8.4
Flash point ºC	140ºC
Vapor Pressure (hPa)@25ºC	0.013
Molecular weight	239 - 245
Octanol Water Partition Coefficient (log K_{ow})	7.5 – 9.12 @25ºC
Half-life	12 – 15 days

Reference : National Institute of Occupational Safety and Health Guide to Chemical Hazards and International Chemical Safety Cards (WHO/IPCS/ILO), 2011.

Moreover, Murray *et al* (1991) observed that total LABs in K_{bcd} (bioconcentration dry) and K_{bcl} (bioconcentration lipid) were 0.50 to 0.69 x 10^6 and 3.4 to 4.0 x 10^6 respectively.

1.4.3. Synthesis of LABs

LAB, the precursor of LAS, is manufactured in large scale industrial processes by alkylating benzene with linear mono-olefin or alkylhalides such as chloro-paraffins by using HF or $AlCl_3$ as the alkylation catalyst (Cavalli *et al* 1999b), and recently also over heterogeneous solid super-acids in a fixed-bed reactor (Erickson *et al* 1996). Alkylation with $AlCl_3$ was the first commercial process used in the mid 60s when branched dodecylbenzene (DDB) was replaced by LAB. At the end of the 60s the HF technology was applied for the first time and immediately it became the preferred technology to be installed in the world to produce LAB. In the mid 90s a new alkylation technology based on heterogeneous catalyst in a fixed-bed reactor, appeared on the market (Berna *et al* 1994) and was rapidly adopted, as testified by several new units recently installed with this technology. The new technology offers considerable advantages over the old ones, namely: process simplification, elimination of acids handling and disposal (HF, HCl) as well as an overall production yield improvement and improved LAB quality.

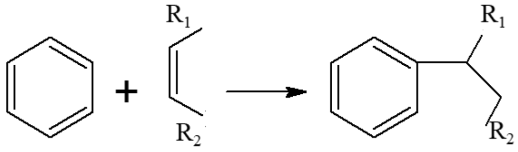


Figure 1.16. Reaction of LAB formation

On the other hand, Thoumelin, 1995 proposed that the synthesis of these compounds is carried out in two main stages. Firstly, linear alkylbenzene hydrocarbons (LAB) are formed. This is usually done by catalytic alkylation of benzene (Friedel-Crafts alkylation) from olefin which generally has 10 to 14 carbon atoms. Alkylation of benzene occurs simultaneously with isomerization of the olefin by displacement of the double bond. This results in a statistical distribution of benzene rings along the paraffinic chain, with the exception, however, of terminal carbons. In a second step, the LABs are sulphonated using concentrated sulfuric acid or by pressurized SO_3, currently the most widespread method. This reaction is so-called electrophilic substitution on an aromatic moiety.

A homologue may be characterized by a formula in $C_{n,\ n}$ denoting the number of carbons of the alkyl chain, generally between 10 and 14. For each homologue, there are different isomers that can be characterized by a formula in $_m C_{n,\ m}$ being the carbon number of the alkyl chain to which the benzene ring is connected (m = 2, 3, ...n / 2 if n even, m = 2.3, ...n / 2 + 1 if n odd). Isomers that have a benzene ring attached to a carbon near the end of the alkyl chain are often referred to as "outer" isomers as opposed to "internal" isomers that have a benzene ring connected to a carbon located in the middle of this chain.

LAB as the biodegradation products of LAS is produced in numerous scale industrial processes through alkylating benzene with linear mono-olefins or alkyl halides such as chloro-paraffins by employing HF or $AlCl_3$ as the alkylation catalyst (Cavalli *et al* 1999b), and recently also over heterogeneous solid super-acids in a fixed-bed reactor (Erickson *et al* 1996). The quality of these compounds, as measured by its bromine and color indexes as well as by impurities and alkyl chain linearity, has been increased over time following significant technological improvements (Marr *et al* 2000). Alkylation with $AlCl_3$ was the first commercial process used in the mid 60s when branched dodecylbenzene (DDB) was replaced by LAB. At the end of the 60s the HF technology was applied for the first time and immediately it became the preferred technology to be installed in the world to produce LAB.

In the mid 90s a new alkylation technology based on heterogeneous catalyst in a fixed-bed reactor, appeared on the market (Berna *et al* 1994) and was rapidly adopted, as testified by several new units recently installed with this technology. The new technology offers considerable advantages over the old ones, namely: process simplification, elimination of acids handling and disposal (HF, HCl) as well as an overall production yield improvement and improved LAB quality.

The result of sulphonating LAB is the formation of alkylbenzene sulphonic acid, which has the consistency of a liquid with a high active content, >97% by titration with hyamine (ISO 2271; EN 14480), containing about 1% of unsulphonated matter and 1 - 2% of H_2SO_4 (IUCLID 1994; Schönkaes 1998). It represents commercially the most important supply form. The acid is then neutralised with a base to give the final LAS surfactant salt. Sodium neutralised LAS is by far the predominant grade. As salt, it can also be supplied in various forms and active contents, for example as paste (50 - 75%) and powder (80 - 90%) (Schönkaes 1998).

1.4.4. Use

LAB is anionic surfactant which is by the sulfonation processes can be produced linear alkylbenzene sulfonate that is able to biodegrade. Linear alkylbenzene sulfonate (LAS) has replaced the branched one (dodecylbenzene sulfonates) which was banned due to their slowly biodegrade.

Higher n-olefins of C_8–C_{14} are used as intermediates in the manufacture of several types of surfactant materials. Linear internal olefins are used in the production of linear alkylbenzene; alkylphenol; detergent alcohols, which in turn is used to produce alcohol sulfates, alcohol ethoxylates, and alcohol ether sulfates; and synthetic lubricants. α-Olefins are used in the production of detergent alcohols, linear alkylbenzene, synthetic lubricants, and α-olefin sulfonates (another ionic surfactant).

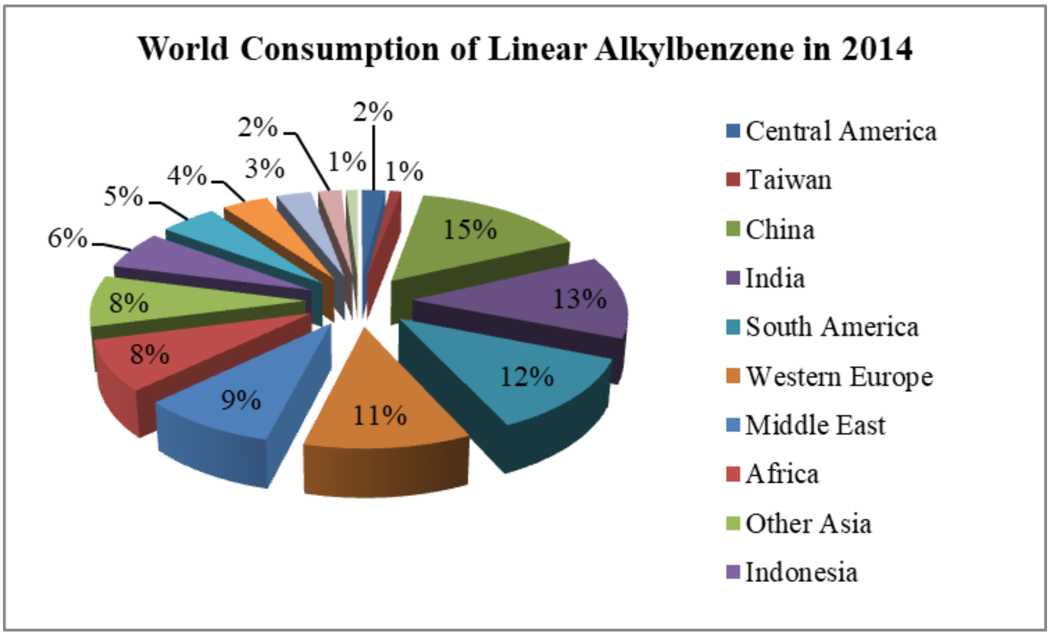


Figure 1.17. World Consumption of linear alkylbenzene in 2014
Source: Chemical Economics Handbook, April 2015

Over the forecast period, demand is expected to increase at an average annual rate of almost 2.5%, albeit with significant regional differences (Figure 1.17). Growth will be driven by healthy demand in India, China, and Indonesia. These three countries consumed 40% of total world LAB demand in 2014. In 2014, consumption of LAB in India was nearly equal to LAB consumption in China. By 2019, consumption of LAB in India is projected to surpass that of China. India still uses a lot of powder detergents whereas liquid detergents are growing in China. If crude oil prices (and consequently the prices of LABs raw materials n-paraffins and benzene) increase significantly during 2014–19, global consumption will likely grow closer to 2%. Additionally, if there is a big switch to competing oleochemical-based surfactants (particularly in the developing regions and primarily as a result of possible lower fatty alcohol prices in the future compared with LAB), this will also negatively affect LAB consumption, as countries like China will switch detergent formulations.

In mature markets, like North America, Western Europe, and Japan, consumption will be slightly declining, flat, or slightly increasing at best. This is a result of the efforts of detergent manufacturers to introduce new products that contain less surfactant per wash load. In recent years, liquid laundry detergents have become more popular with consumers, and therefore, consumption of powder laundry detergent (traditionally containing significant amounts of LAS) has been decreasing. On the other hand, regions with still-developing markets, with significantly lower consumption of detergents per capita, like Asia, Central and South America, the Middle East, and Africa, are expected to register an increase in demand between 2% and 4% annually.

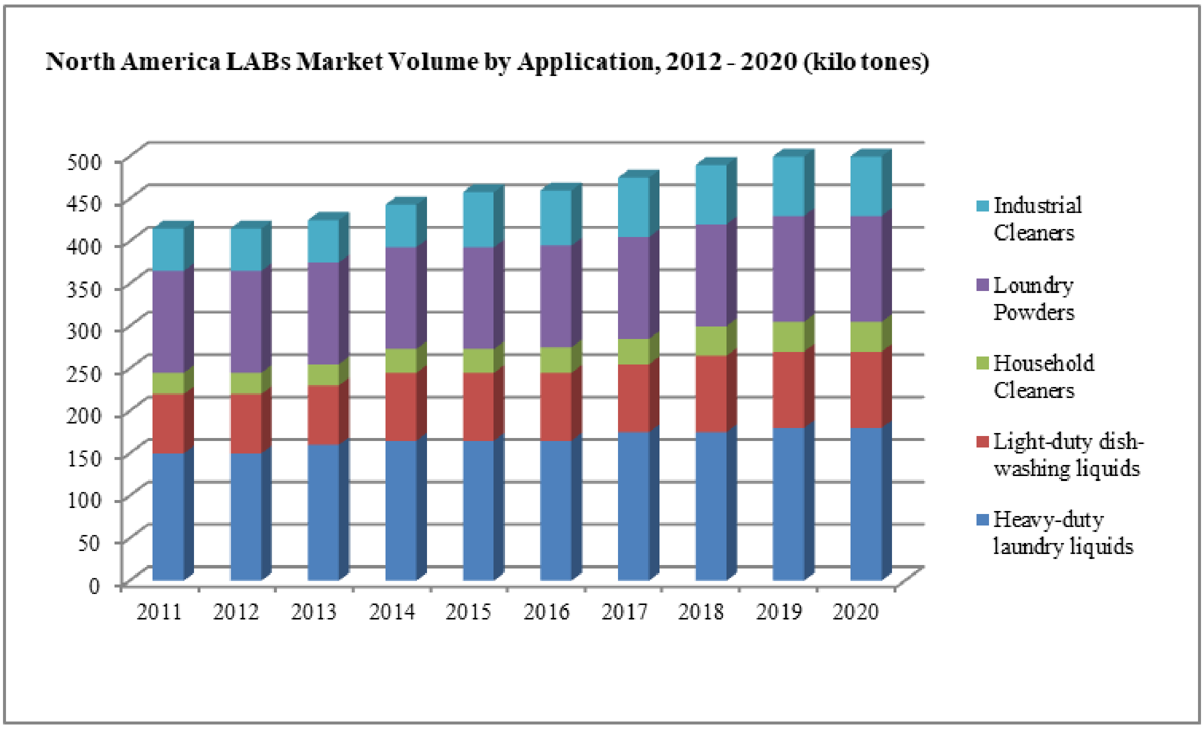


Figure 1.18. Linear alkylbenzenes (LABs) market volume by application, 2012 - 2020 (Kilo Tons) in North America (Source: Grand view research, 2015).

On the other hand, it is forecasted that the application of LABs in several human needs in North America as shown in Fig.1.18 increase slightly to 2020. The most uses of these chemicals were to heavy duty laundry cleaner. Meanwhile, the least employs of the substances were to household cleaner.

According to this information, the compounds would extend in the environment particularly in marine area as long as people use intensively LABs in their daily life. Should it not carried out an intensive study related with the fate and occurrence of LABs, it cannot be avoided that there will be the adverse effects, not only to the marine benthic organisms but also human beings in the future.

1.4.5. Sources, transport and fate of LABs

Urban areas, as the most populated places, are unavoidable to be the heavy anthropogenic impacts on the environment at various scales (Hardoy *et al* 2001; Grimm *et al* 2008; Marcotullio *et al* 2008; Wei *et al* 2014). Soil, as a solid environmental matric, is considered as the principal sink of contaminants produced by human activities (Wild *et al* 1990; Wild and Jones 1995), hence, it could be the indicator to descript anthropogenic tracers. As a results of human activities in the terrestrial domain, it causes multiple pollutants derived from many sources (Doney 2010) that are able to be transferred through numerous of routes like hydrodynamics (currents, wave and tides in the ocean and rivers) and the aerial transport that can pose the impacts even on the distant areas from points of discharge (Heywood *et al* 2006; Nam *et al* 2009; Wei *et al* 2014).

It is important to mention that LABs, unlike PAHs, are exclusively derived from anthropogenic sources such as domestics, industrial activities and wastewater treatment plant. In this regard, LABs are mainly linked with the production of linear alkylbenzenes sulfonates (LAS) (Eganhouse *et al* 1983; Wei *et al* 2014), one of the most extensively employed anionic detergents and surfactants.

Linear alkylbenzenes could be emitted into the environment as the remaining parts (1 – 3%) of the detergents that are traded (Hartmann *et al* 2000; Eganhouse and Sherblom 2001; Heim *et al* 2004; Isobe *et al* 2004; Wei *et al* 2014). These chemicals have detected in the different environmental matrices from various area throughout the globe. In the sediments (Wang *et al* 2014; Alkhadher *et al* 2015; Muniz *et al* 2015; Venturini *et al* 2015; Dwiyitno *et al* 2016; Masood *et al* 2016; Moreira *et al* 2017) in soils (Holt and Bernstein 1992; Johnson *et al* 2007; Wei *et al* 2014) in atmospheres (Schnelle-Kreis *et al* 2005) and in the biotas (Murray *et al* 1991; Serrazanetti *et al* 1994; Widdows *et al* 2002; Dwiyitno *et al* 2016).

Riverine overflows were considered as the predominant media for transferring these substances from sources to the marine ecosystems (Luo *et al* 2008; Ni *et al* 2008). Moreover, the irrigation system with contaminated fluvial water was suggested as the essential input type for LABs in the areas where agricultural activities undergone (Ni *et al* 2009). However, Wei *et al* 2014 revealed that by using soil linear alkylbenzenes (LABs) as the indicators of anthropogenic influences, emphasizing on the role of atmospheric transport in dissipating these substances from input sources to remote areas. They discovered that atmospheres as an important route and more viable dissipating mechanism for these chemicals.

1.4.6. The alteration in the Environment

These chemicals with 10 to 14 carbon atoms of normal alkyl chain are categorized as a group of raw materials to produce linear alkylbenzenesulfonates (LAS) which eventually are employed as nonionic surfactant for manufacturing commercial detergents (Almeida *et al* 1994). Since these important residual phenylalkanes in commercial detergents could be emitted into natural water with domestic wastewater and are considerably resistant to degradation, they are often considered as indicators of anthropogenic activities and particularly they have been widely used as molecular markers of sewage discharge (Eganhouse *et al* 2000; Martins *et al* 2010).

LAB components are often expressed as i-Cn, where n indicates the number of carbon atoms (usually, n ranged from 10 to 14) in the alkyl chain and i, indicates the position of the phenyl. Since internal isomers with phenyl positions at the middle of the alkyl chain are more resistant to biodegradation than external isomers (Takada and Eganhouse, 1998) and LAB homologues with shorter alkyl chains (C_{10}-LABs and C_{11}-LABs) are easier to be depleted than the longer-chain homologues (C_{12} and C_{13}-LABs) (Luo *et al* 2008), isomer- and homologue-selective biodegradation of LABs may occur in the environment. Therefore, the compositional distribution of LABs is valuable for assessing the degree of biodegradation of LABs and consequently the degree of sewage treatment. In addition, LABs may also be employed to trace other organic pollutants with similar physicochemical properties (Ni *et al* 2009).

The relative abundances of LAB isomers in the commercial detergents and raw sewage are stable (Takada and Ishiwatari 1987); however, changes in isomeric composition have been observed in treated wastewater and coastal sediment due to selective biodegradation (Isobe *et al* 2004). I/E ratio, ΣC_{13} - LAB/ΣC_{12} - LAB and L/S have been employed widely as indicators of LAB degradation (Gustafsson *et al* 2001; Luo *et al* 2008). The I/E values in commercial detergents and untreated sewage were lower than or close to 1; however, it was higher than 1 in coastal sediment, treated sewage or aquatic biological tissue due to preferable biodegradation of the external isomers relative to the internal isomers (Takada and Eganhouse, 1998). The results from an incubation experiment conducted by Takada and Ishiwatari (1990) suggested that the percentage of degradation was exponentially increased with increasing I/E. Similarly, the values of ΣC_{13} - LAB/ΣC_{12} - LAB and L/S in detergent and untreated sewage were significantly lower than those in river water (Ni *et al* 2008) and sediment (Luo *et al* 2008) due to the selective degradation of long-chain alkylbenzenes relative to short-chain ones.

Several works compared these biodegradation degrees from some different matrices and they proved that the value of I/E in the environmental samples varied from 0.8 to 2.1 with a mean of 1.1 ± 0.3 which were similar to those in commercial detergents (Luo *et al* 2008; Ni *et al* 2008), and significantly lower than those found in sludge (Luo *et al* 2008) and suspended particles from wastewater (Takada and Ishiwatari, 1987). Furthermore, they explained that low I/E values were probably due to recent inputs of untreated or inadequately treated wastewater effluent. Beside, weak biodegradation of LABs occurred in sediment probably due to its anaerobic conditions. Study showed that anaerobic conditions suppressed the degradation of LABs (Takada and Ishiwatari 1990). Therefore, the anaerobic conditions may have limited the biodegradation of LABs.

Many studies have been conducted to isolate and identify bacterial species responsible for the degradation of these surfactants. Swisher (1987), referring to the results published in the literature, lists about 90 species able to develop from surfactants, for instance LABs. Many of them are commonly found in the natural environment. They belong particularly to the genera of *Pseudomonas*, *Aerobacter* and *Alcaligenes*. The genera *Flavobacterium*, *Micrococcus* and *Bacillus* have also been cited for the degradation of these substances (Cabridenc 1988). Bacteria capable of degrading LABs and belonging to the genera *Pseudomonas* and *Alcaligenes*, or *Oceanospirillum* and *Alteromonas* have been isolated in coastal waters of Mediterranean (Sigoillot 1987). From a general point of view, it appears that mixed (multispecific) crops have a higher degradation potential than pure (monospecific) crops.

1.4.7. Toxicity

Unlike PAHs, we have lack information on the toxicity of LABs particularly in marine organisms. Like others hazard compounds, they have found in high concentrations in aquatic organisms such as mussel and fish due to poorly treated of sewage discharged (Albaiges *et al* 1987; Murray *et al* 1991; Sherblom *et al* 1991; Serrazenetti *et al* 1997; Tsutsumi *et al* 2002; Venkatesan *et al* 2002). Meanwhile (Robinson and Schroeder 1992) investigated terrestrial animal such as rats which has adverse effects during their developmental and reproductive periods when they were exposed to certain concentrations of these chemicals.

Several studies have analyzed the concentrations containing of LABs within marine sediments in high concentrations, adjacent to urban and industrial centers and linked their sources to municipal wastewater (Rinawati *et al* 2012; Wang *et al* 2012; Venturini *et al* 2015; Dwiyitno *et al* 2016) which might induce adverse effects to the benthic ecosystem.

LABs will be indicated to be toxic in which the acute toxicity of LABs to *Caenorhabditis elegans* in soil was revealed a lethal concentration of 1550 ng.g^{-1} to cause 1% fatality in 24 h, with the 95% confidence limits in the range of 80 – 3360 ng.g^{-1}. Due to these characteristics, these compounds are the good indicators of human activities particularly linked with sewage contamination in various areas throughout the globe (Wei *et al* 2014).

To date, there has not been data on human impacts to these LABs exposition via various route such as inhalation, dermal contact and ingestion. However, as the aerial deposition was hypothesized as an essential input route for soil LABs in forestry and drinking water sources area with little impact of irrigation or direct wastewater discharge, it could be impacted to human and animal in the vicinity of the area through these medias (Wei *et al* 2014).

Nevertheless, these emerging pollutants could affect the rats dermal with LD_{50} of > 2000 $mg.kg^{-1}$ and through inhalation with LC_{50} of > 1.82 $mg.l^{-1}$. Slight irritation could occur to the rabits (SEEF 2014). Additionally, Robinson and Schroeder 1992 found that at the concentrations of 125 mg/kg/day can cause adverse effects to the reproductive and developmental of rat. Whereas, Jhonson et al 2007 reported that the acute toxicity of LABs to *Caenorhabditis elegans* in soil as a lethal concentration of 1550 $ng.g^{-1}$ to cause fatality in 24 h, with 95% confidence limits in the range of 80 – 3360 $ng.g^{-1}$.

1.4.8. The occurrence of LABs in sediments throughout the World (1992 to 2017).

We have studied 31 articles published on scientific journal around the globe which content a comprehensive data on Linear Alkylbenzenes (LABs) concentration levels in marine and several river sediments was gathered (Table 1.13). The resulting time trends for emissions and concentrations measured in the aquatic system itself are presented. The data are available at least during 25 years from 1992 to 2017 which categorized as chronicle pollution namely the pollutions which are emitted intensively from the sources like wastewater treatment plant and sewage discharged to the environment. Whereas, punctual pollutions are pollutions that emitted to the environment from various sources such as industrial, urban or domestic activities.

In this work, we clustered the data from three periods of the time. First, the period of 1992 to 1995 where the magnitude of LABs concentration levels in the sediments recorded ranged between 1 $ng.g^{-1}$ in the sediments connecting to the sewage and dumpsite area of Deep-Ocean Dump Site off New York, US (Bothner *et al* 1994) and 421 $\mu g.g^{-1}$ from the effluent of Joint Water Pollution Control Plant from St Monica Basin, Southern California, US (Chalaux *et al* 1992). Subsequently, the periods of 2001 to 2010, LABs concentrations ranged between 1 $ng.g^{-1}$ from ex-heavy industrial area of Lippe River, Germany to 42.6 $mg.g^{-1}$ from industrial and urban area (Heim *et al* 2004) of South and Southeast Asia (Isobe *et al* 2004). Recent works observed these chemicals in sediments of < 0.85 $ng.g^{-1}$ from the area connecting to the sewage discharges of Antarctic Station, Brazil (Martins *et al* 2012) to 330 $\mu g.g^{-1}$ from industrial and urban area of Jakarta Bay, Indonesia (Dwiyitno *et al* 2016).

It can be seen that in the 90's era to the earlier of 2000's the concentrations of LABs underwent a trend which they increased significantly. This high concentration was found in the industrial and urban area in the South and Southeast Asia which indicated that the treatment did not work properly, even some wastes dumped directly to marine area. However, recent work revealed an important decline of LABs concentration to be 330 $\mu g.g^{-1}$ which probably induced by high technology treatment of wastewater treatment plant in some area.

It can be concluded that sludge or the sediments that connecting directly to the sewage discharges do not always emit a high concentration of the pollutants. Contrarily, environmental matrices from urban or industrial area may emit an immense concentration of these pollutants. This analysis reflected that the evolution of LABs concentrations in marine sediments has experienced the important changes during at least three decades.

Table 1.13. The occurrence of LABs in sediments throughout the World (1992 to 2017).

Land Condition	**Concentrations**	**Locations**	**References**
Industrial and domestic wastes discharged	∑LABs = 0.13 - 3.27 µg.g^{-1}	Tokyo Bay, Japan	Takada *et al* (1992)
Dump site	∑LABs = 2.5 - 84.8 ng g^{-1} 0.10 – 2.3 µg.g^{-1}	Coastal area around River Humber, North Sea	Raymundo and Preston (1992)
The effluent of Joint Water Pollution Control Plant	∑LABs = 421 µg.g^{-1} ∑LABs = 6711 - 8730 ng.g^{-1}	St Monica Basin, Southern California, US	Chalaux *et al* (1992)
Connecting to sewage and dumpsite area	∑LABs = 1 – 116 ng.g^{-1} ∑LABs = 90000 – 213000 ng.g^{-1}	Deep-Ocean Dump Site off New York, US	Bothner *et al* (1994)
Municipal and industrial sewage	∑LABs = 0.41 - 23.5 µg.g^{-1}	Xiamen and Victoria Harbor, China	Hong *et al* (1995)
Connecting to treated and untreated wastes	∑LABs = 146 µg.g^{-1} 0.65 ∑LABs = 24.5 µg.g^{-1}1.63	Tokyo Bay, Japan	Chalaux *et al* (1995)
Effluent of a large combined sewer overflow	∑LABs = 4 - 55 µg.g^{-1}	Boston Harbor, US	Eganhouse and Sherblom (2001)
Connecting to Hyperion Treatment Plant (HTP) outfall	∑LABs = 848 – 61.500 ng.g^{-1}	Santa Monica Bay, California, US	Bay *et al* (2003)
Oil terminal and tourist resort	∑LABs = 12.6 - 27.7 ng.g^{-1}	Sao Paulo State, Brazil	Medieros and Bicego (2004a)
Petrochemical and metallurgical industrial areas	∑LABs = 16.9 - 430.6 ng.g^{-1}	Santos Bay and Estuary, Brazil	Medieros and Bicego (2004b)
Connecting to wastewater discharges	∑LABs = 17.4 - 32.0 ng.g^{-1}	Southern California Bight, US	Macıas-Zamora and Ramırez-Alvarez (2004)
Heavy industrial area in the past	∑LABs = 1 – 203 ng.g^{-1}	Lippe River, Germany	Heim *et al* (2004)
Industrial and urban area	∑LABs = 0.002 – 42.6 mg.g^{-1}	South and Southeast Asia	Isobe *et al* (2004)
Petroleum distributor and refinery, shipping activities and sewage outfalls	∑LABs = 3.2 - 1601.9 ng.g^{-1}	Patos Lagoon Estuary, Brazil	Medieros *et al* (2005)
Industrial and sewage discharge	∑LABs = 18 µg.g^{-1}	Buenos Aires coastal area, Argentina	Colombo *et al* (2007)
Connecting to sewage system	∑LABs = <1.0 to 23 ng g^{-1}	Admiralty Bay, King George Island, Antarctica	Montone *et al* (2010)
Industrial and sewage disposal	∑LABs = 0.1 – 10 µg.g^{-1}	Santa Monica Bay, California, USA	Venkatesan *et al* (2010)
Discharge of untreated industrial effluents and domestics wastes	∑LABs = 4.7 - 1344 ng.g^{-1}	Santos Estuary, Southeastern Brazil	Martins *et al* (2010)

Industrialization, urbanization, and motorization area	$\sum$LABs = 1400 ng g^{-1}	Jakata Bay, Indonesia	Rinawati *et al* (2012)
WWTPs discharge	$\sum$LABs = 18.5 - 5720 ng g^{-1}	Chaohu Lake, China	Wang *et al* (2012)
Industrial and sewage discharge	$\sum$LABs = 1.5 – 410 ng.g^{-1}	Dongjiang River, China	Zhang *et al* (2012)
Sewage discharged	$\sum$LABs = <1.0 - 46.5 ng.g^{-1}	Antarctic Station, Brazil	Martins *et al* (2012)
Industry and urban area	$\sum$LABs = 37 - 168 ng.g^{-1}	Santos-São Vicente Estuarine System, Southern Brazil	Buruaem *et al* (2013)
Connecting to sewage input	$\sum$LABs = 413.3 ng.g^{-1}	Babitonga Bay, Brazil	Martins *et al* (2014)
High industrialization and urbanization	$\sum$LABs = 5.6 - 77 ng.g^{-1}	Continental shelf, China and Taiwan	Wei *et al* (2014)
Connecting to Wastewater	$\sum$LABs = 10.3 - 110 ng g^{-1}	Huaihe River, China	Wang *et al* (2014)
Urban area	$\sum$LABs = 7.1 - 41.3 ng g^{-1}	Brunei Bay	Alkhadher *et al* (2015)
Connected to domestic sewage	$\sum$LABs = 76.3 - 7779 ng g^{-1}	Río de la Plata Estuary, SW Atlantic, Argentine and Urugay	Venturini *et al* (2015)
Near sewage outfall	$\sum$LABs = below DL–51.3 ng.g^{-1}	São Sebastião Channel, SP, Brazil	Muniz *et al* (2015)
Connecting to municipal wastewater	$\sum$LABs = 23.7 - 113.3 ng.g^{-1}	Kuala Selangor, Malaysia	Masood *et al* (2016)
Industrial and urban area	$\sum$LABs = 20 ng.g^{-1} - 330 μg.g^{-1}	Jakarta Bay, Indonesia	Dwiyitno *et al* (2016)
Effluent discharge oil refinery	$\sum$LABs = <0.85 - 5.84 ng.g^{-1}	Semi-arid region, Brazil	Moreira *et al* (2017)

LAB = Linear alkylbenzenes, WWTPs = wastewater treatment plants

1.4.9. Review of Analytical Methods (1992 to 2017)

The analytical methodologies of organic micro-pollutants, particularly Linear Alkylbenzenes in the sediments analysis have not been changed significantly for at least three decades. Although, there were some differences in the analysis caused solely by the differences of the availability of the equipment in the laboratory. These days, the development and optimization of integrated analytical approaches based on the different techniques to study at the concentration levels of the chemical compositions of the environmental matrices to define the contamination degrees, valuable to assess environmental values, safety, quality and authenticity. This comprehensive strategy includes emerging pollutants area such as linear alkylbenzenes to meet an advanced analytical technique. Integrated approaches can help to elucidate some critical issues in organic micro-pollutants analysis particularly in marine area, but also to face the new challenges of globalized world security, sustainability and marine resources production in response to environmental worldwide changes. They include the development of powerful analytical methods to ensure the origin and quality of the data, as well as the discovery of biomarkers to identify potential safety of the environmental area. Far from the aim of an exhaustive review of the abundant literature, we explored how classical approaches, such as those used in several target compounds such as PAHs, PCBs, and Pesticides have evolved to intersect with the new technology to produce a progress in our understanding of the complexity of the environmental problems. Perhaps most importantly, a key objective of the review will be exploring the development simple and robust methods for a fully applied of the data in environmental science.

We have reviewed 31 articles that have been published on several scientific journals throughout the world for at least more than two decades (25 years) from 1992 to 2017 (Table 1.14). The period of 1992 to 1995, mostly, people employed soxhlet with dichloromethane and methanol as solvents extraction (Raymundo and Preston 1992; Takada *et al* 1992; Chalaux *et al* 1995). Meanwhile, samples purification used glass column chromatography to separate the target compounds and elution using n-hexane (Chalaux *et al* 1995; Hong *et al* 1995). We recorded the identification of linear alkylbenzenes at the time used various instruments such as GC-FID, GC-MS and GC-ECD. The accuracies of the methods developed were sufficient with the recoveries ranged between 50 to 85% despite Takada *et al* 1992 reported their method was uncorrected and Chalaux 1995 did not report their method performances.

Subsequently, during the period of 2001 to 2007, sample extractions were predominated by soxhlet with the same solvents as the investigators did for the previous period. Several works used shaker (Eganhouse and Sherblom 2001), microwave (Bay *et al* 2003), high speed dispersion device (Heim *et al* 2004) and ultrasonic (Colombo *et al* 2007). The fractionation still used silica glass column to separate the compounds from the sediments. Despite some of works used others devices such as HRGC-MS (Eganhouse and Sherblom 2001) and HRGC-FID-ECD, HRGC-MSD (Colombo *et al* 2007) to identified LAB most of works employed GC-MS. The accuracies of these methods were reliable due to the recoveries ranged between 65 to 88%. Unfortunately, a few of studies did not report their performance (Bay *et al* 2003; Heim *et al* 2004; Medieros and Bicego 2004a,b; Medieros *et al* 2005).

Recently (2001 to 2017), the analysis of LABs has not been undergoing any significant evolution. It can be seen from the sample extractions still used soxhlet apparatus despite of time and solvents consuming. Whereas the identification of the compounds dominated by GC-MS as that of the previous periods. The recoveries of these methods developed ranged between 50 – 137% which were the excellent results.

Table 1.14. Review of analytical methods (1992 to 2017)

Extraction	**Purification**	**Identification**	**Performance**	**References**
Soxhlet-extracted with benzene-methanol, florisil column to remove copper and polar material1	Column chromatography using alumina and silica. elution with n-hexane	GC-FID	Uncorrected recoveries	Takada *et al* (1992)
Soxhlet with dichloromethane-methanol	Silica gel column chromatography	GC-MS	Recoveries = 72.8±7.6 - 83.52±6.6%	Raymundo and Preston (1992)
Virtis homogenizer using methanol and Dichloromethane, solvent exchanged to hexane	Silica-alumina column chromatography, Elution with n-hexane	GC-MS	Recoveries = >70%	Chalaux *et al* (1992)
Extracted with cyelohexane	Fractionation using silica Gel alumina, elution with n-hexane	GC-ECD	Recoveries = 50 - 85% MDL = 0.1 – 1 ng.g^{-1}	Hong *et al* (1995)
Soxhlet-extracted dichloromethane-methanol	Alumina column chromate, DCM/hexane, elution with hexane.	GC-FID GC-MS	Unreported	Chalaux *et al* (1995)
Shaker table using	Silica gel column	HRGC-	Recoveries = 74.9±12.7% -	Eganhouse and

dichloromethane/methanol	chromatography	MS	85.6±8.1% MDL = 0.5 to 10.7 ng.g^{-1}	Sherblom (2001)
Microwave-assisted solvent extractor (methylene chloride 3 x)7	Fractionation column chromato	GC–MS	Unreported	Bay *et al* (2003)
High speed dispersion device (Ultra Turrax, T25, IKA, Stauffen, Germany) and centrifugation (Acetone/hexane)	Fractionation using silica Gel (pentane/dichloromethane)	GC-MS	Unreported	Heim *et al* (2004)
Soxhlet apparatus with dichloromethane/methanol	Fractionated using two-step silica gel column chromatography	GC-MS	Recoveries = 83 - 109%	Isobe *et al* (2004)
Soxhlet dichloromethane solvent exchanged to hexane	Adsorption liquid chromatography Column alumina and silica-gel, elution with n-hexane	GC-MS	Recoveries = 65±10%	Macıas-Zamora and Ramırez-Alvarez (2004)
Soxhlet n-hexane and dichloromethane	Adsorption chromatography with alumina and silica-gel.	GC-MS	Unreported	Medieros and Bicego (2004a)
Soxhlet with n-hexane/ Dichloromethane	Adsorption liquid chromatography Column alumina and silica-gel, elution with n-hexane	GC-MS	Unreported	Medieros and Bicego (2004b)
Soxhlet with n-hexane/dichloromethane	Adsorption liquid chromatography Column alumina and silica-gel, elution with n-hexane	GC-MS	Unreported	Medieros *et al* (2005)
Ultrasonic (acetone, dichloromethane, petroleum ether)	Nitrogen concentration, copper treatment, silica gel fractionation	HRGC-FID-ECD and HRGC-MSD	Recoveries = 75±12%	Colombo *et al* (2007)
Soxhlet-extracted with hexanes/ Dichloromethane	Silica gel-alumina column chromatography (hexane/DCM)	GC–MSD	Recoveries = 78 to 88%. MDL = 0.03 to 1.37 ng g^{-1}	Montone *et al* (2010)
Sonication with methanol and methylene chloride, Desulphurization with activated copper	Column chromatography using alumina and silica. elution with n-hexane	GC-MS	MDL = 0.05 - 0.1 ng.g^{-1}	Venkatesan *et al* (2010)
Soxhlet hexanes and dichloromethane	Adsorption liquid chromatography with alumina and silica gel column. Eluted with hexanes	GC-MS	Recoveries = 78.1 to 88.2%. MDL = 0.03 to 1.37 ng.g^{-1}	Martins *et al* (2010)
Soxhlet dichloromethane, acetone, solvent exchanged to n-hexane	Glass column alumina silica, eluted with hexane	GC-MS	Recoveries = 86±19%	Zhang *et al* (2012)
Soxhlet extraction methylene chloride for 48 h. Desulphurization with activated copper.	Glass column alumina silica, eluted with hexane	GC-MS	Recoveries = 74.7% to 137%	Wang *et al* (2012)

solvent-exchanged to hexane				
Soxhlet extracted with hexanes/dichloromethane	Adsorption liquid chromatography with alumina and silica gel column. Eluted with hexanes	GC-MS	Unreported	Martins *et al* (2012)
ASE DCM/Acetone	Two step of silica gel column chromatography	GC-ECD	Recoveries = 82% to 106%	Rinawati *et al* (2012)
Soxhlet-extracted n-hexane and dichloromethane	Silica gel-alumina column chromatography, elution with n-hexane	GC-MS	Recoveries = 88.5% to 109% LOQ = 2.5 - 3.0 ng.g^{-1}	Buruaem *et al* (2013)
Soxhlet dichloromethane, acetone, solvent exchanged to n-hexane	Glass column alumina silica, eluted with hexane	GC-MS	Recoveries = 84 ± 15%	Wei *et al* (2014)
Soxhlet extraction using acetone and hexane Desulphurization performed by activated copper	Glass column alumina silica, eluted with hexane	GC-MS	Recoveries 83.3% to 137%	Wang *et al* (2014)
Soxhlet extracted dichloromethane (DCM) and n-hexane	Adsorption liquid chromatography Column alumina and silica-gel, elution with n-hexane	GC-MS	Unreported	Martins *et al* (2014)
Soxhlet extracted mixture of dichloromethane and n-hexane	Column chromatography using alumina and silica. elution with n-hexane	GC-MS	Recoveries 60 = % to 110% LOD = 0.85 – 1.68 ng.g^{-1}	Venturini *et al* (2015)
Soxhlet-extracted with hexane/dichloromethane	Liquid chromatography alumina and silica gel column. Eluted using hexane	GC-MS	Recoveries = 52 to109% MDL = 0.03 to 1.37 ng.g^{-1}	Muniz *et al* (2015)
Soxhlet-extracted using 250 mL of high purity dichloromethane	Silica gel column chromatography, elution with hexane/DCM	GC–MS	Recoveries = 82–104%	Alkhadher *et al* (2015)
Soxhlet distilled dichloromethane (DCM)	Silica gel column chromatography	GC-MS	Recoveries = 78.1% to 88.2%	Masood *et al* (2016)
High speed dispersion tool (Ultra-Turrax T-25 basic, IKA-Werke, Staufen, Germany) of acetone and n-hexane30	Column chromatography with activated silica gel using mixtures of n-pentane, dichloromethane and methanol	GC-MS	Recoveries = 50%	Dwiyitno *et al* (2016)
Soxhlet (n-hexane and dichloromethane)	Silica gel-alumina column chromatography.	GC-MS	Recoveries = 88.5% to 109%	Moreira *et al* (2017)

DCM = dichloromethane, GC/MS = gaz chromatography/mass spectrophotometry, GC/MSD = gaz chromatography/mass selective detector, GC/FID = gaz chromatography/flame ionization detector. GC/ECD = gaz chromatography/electron capture detector, LOD = limit of detection, HRGC/ECD = high resolution gas chromatography/electron capture detector, MDL = method detection limit, HRGC-FID-ECD = high resolution gas chromatography/flame ionization detector/electron capture detector, HRGC-MSD = high resolution gas chromatography/mass selective detector

1.5. Alkylphenols (APs)

1.5.1. Presentation / Structure / nomenclature

Alkylphenols are truly lipophilic and persistent compounds which are tended to be accumulated in the environment, particularly in sediment and soil. Due to the wide-spectrum of uses and the lack of appropriate treatment in wastewater treatment plants (WWTPs), these chemicals are ubiquitous in the environment (INERIS 2005).

It is well-known that APs are the problematic compounds to the environment, therefore several comercial constituents such as 2,4,6-tri-tert-buthylphenol, nonylphenol (NP) and octylphenol are included in OSPAR priority list of toxic compounds to the marine environment (Maguire, 1999). Additionally, these substances are part of the list of 33 priority chemicals established by the European Water Framework Directive (daughter directive, 2008). Similarly, they are also listed in the "List of Undesirable Substances" (LOUS 2009, 2011) of the Danish Ministry of the Environment.

The lack of the data and the information concerning these APs in the list of the priority studies that have been carried out and the high probability of their discovery in the study area (emisary point of WWTPs) have attracted a systimatically work, including our recent study.

The alkylphenols are phenol derivatives for which one or more of the hydrogen atoms of the aromatic ring have been substituted by alkyl chains (Figure 1.19).

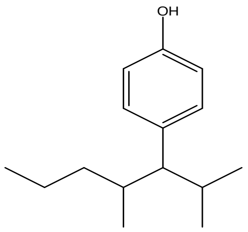


Figure 1.19. Chemical structure of 4-nonylphenol or 4-(2,4-dimethylheptane-3- yl)phenol

The alkylphenols can be synthesized according to 4 major industrial concerned (Figure 1.20), (A) direct alkylation of phenol, (B) hydroxylation of an alkylbenzene, (C) Dehydrogenation of an alkylcyclohexanol, or (D) Cyclization of suitable acyclic compounds

These reactions take place in an atmospheric (or sub-atmospheric) pressure, in the presence of a catalyst such as a Lewis acid for instance boron trifluoride (BF_3), or in the presence of a styrene-type cation exchange resin. divinyl benzene and in batch or continuous reactors (Zoller and Sosis, 2009). Certain alkylphenol formulations can be used directly at the outlet of the reactor without any other treatment step. However, most of the time, commercial alkylphenols require an additional purification step, often by distillation.

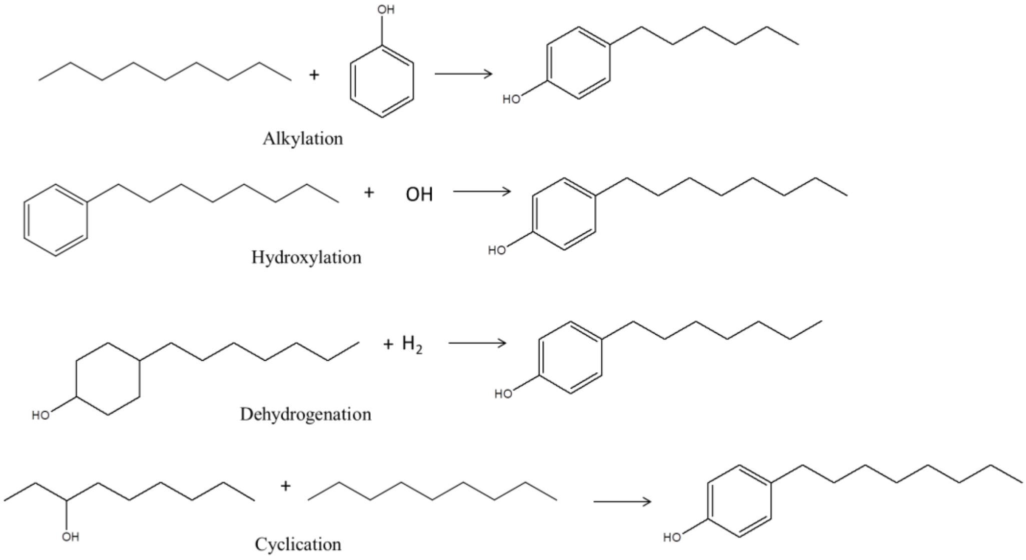


Figure 1 .20. The synthesis of alkylphenols (Zoller et Sosis, 2009)

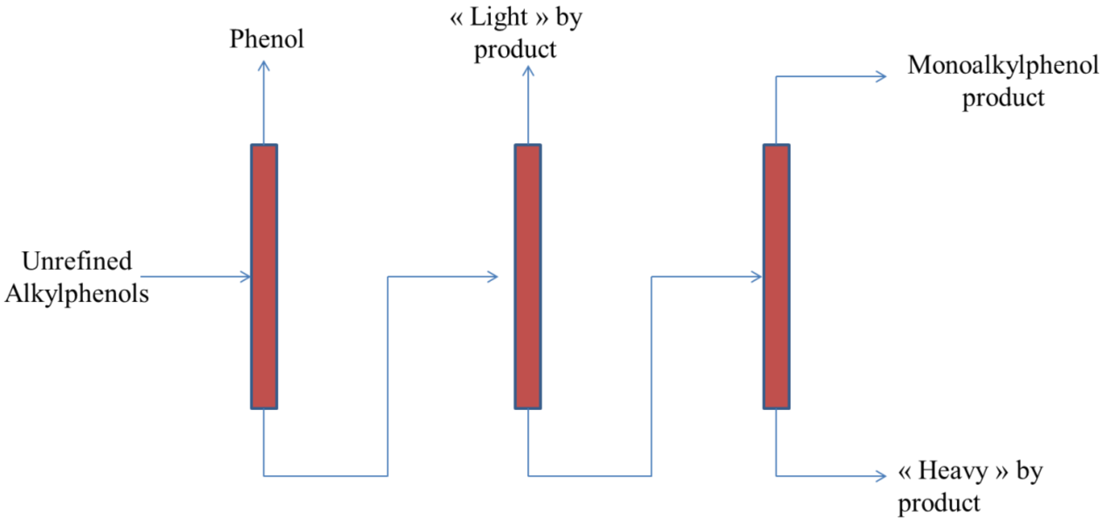


Figure 1.21. The scheme of industrial processes of mono-alkylphenol distillation. (according Zoller and Sosis, 2009).

As illustrated in Figure 1.21, the crude reaction alkylate (Route (A) is introduced into a first distillation column in which excess phenol is taken overhead and recycled to the reaction system. By-products that are more volatile than alkylphenols are eliminated at the top in the second column. The end products are then recovered at the head of the third column, the less volatile final by-products (di-substituted and oligomeric compounds) are withdrawn and removed (Zoller and Sosis, 2009). Despite these purification steps the purities of the commercial products are quite relative as shown in Table 1.15 which presents the current purities of commercial alkylphenols.

Table 1.15. Typical final product purities of APs (Zoller and Sosis 2009)

No	**Product name**	**Minimum Purity (%)**
1	p-*tert*-octylphenol	99
2	p-nonylphenol	90 – 95
3	p-dodecylphenol	90 – 97
4	2,6-Di-Sec-Butylphenol(DSBP)	95
5	Di-nonylphenol	90

Commercial alkylphenols are categorized into three classes : unrefined alkylphenols, mono- and di-substituted alkylphenols, the latter accounting for almost 80% of commercial formulations (Lorenc *et al* 2003) and industrial applications (Warhurst 1995; APERC 2013). Eventually, the most commercially important alkylphenols have alkyl chains of between 1 and 12 carbon atoms in length.

The commercial formulations generally correspond to the complex mixtures of more than one hundred isomers which differ in the structure and branching position of the alkylated chain on the benzene ring (Ieda *et al* 2005).

The nomenclature of monosubstituted alkylphenols (APs) is quite complex and causes many confusions. Although other alkylphenols such as propyl, butyl, pentyl, hexylphenols exist, the term monosubstituted alkylphenol commonly refers to two groups of compounds: nonyl and octylphenols (which will be summarized below by OP and NP, respectively) (Figure 1.22)

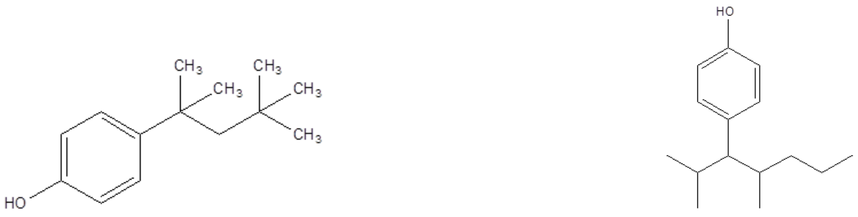


Figure 1.22. Chemical structure of 4-tert-octylphenol (A), 4-nonylphenol (B).

The groups of octyl- and nonylphenol compounds themselves designate many isomeric compounds since the octyl or nonyl group may be branched or linear (n indicating that the chain is linear as 4-n-octylphenol) and located in the 2-positions. - (ortho), 3- (meta) or 4- (para) on the phenolic ring (Figure 1.23).

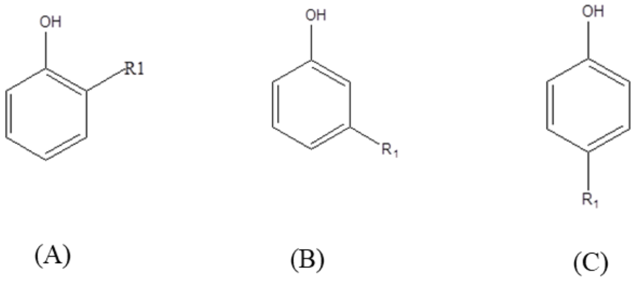
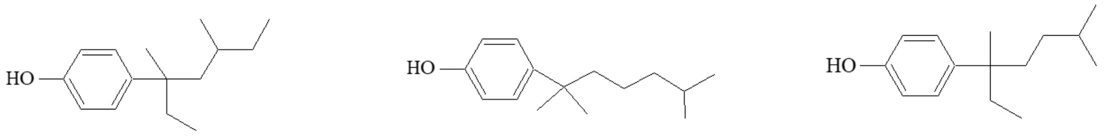


Figure 1.23. The three isomers ; (A) ortho, (B) méta, (C) para of alkylphenols monosubstituted.

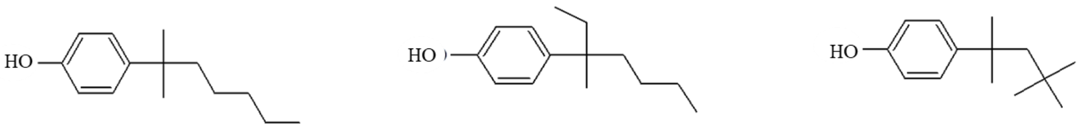
In fact, 90% of the monoalkylphenols present their alkyl radical in the para position with less than 10% in the ortho position (Maguire 1999; Ying *et al* 2002). Moreover, the alkyl chain is often branched due to the existence of different isomers. For example, nonylphenol (monoalkylphenol with an alkyl chain of 9 carbon atoms) is not a pure product but represents a set of isomers (Figure 1.24). Among these different isomers, 4-nonylphenols (4-substituted-branched nonylphenol mixture) represent the vast majority of nonylphenols (around 80%) present in commercial technical mixtures (Ying *et al* 2002). One of the compounds most widely used in commercial formulations is dodecylphenol (monoalkylphenol substituted by a C_{12} alkyl chain), a product also referred to a whole series of isomers. Meanwhile, octylphenol (OP) (C_8 alkyl chain) is a product almost pure, especially 4-tert-octylphenols (OP) because of the particular type of olefin used for its synthesis (Figure 1.24. D), and the other isomers are being minority (Figure 1.24. E and F).



4-(1-ethyl-1, 4-dimethylpentyl)phenol (NP_1)
(A)

4-(1,1,5-trimethylhexyl)phenol (NP2)
(B)

4-1-ethyl-1, 3-dimethylpentyl)phenol (NP_3)
(C)



4-(1,1-dimethylhexyl)phenol (OP)
(D)

4-(1-ethyl-1-methylpenthyl)phenol (OP)
(E)

4-(1,1,3,3 tetramethylbutyl)phenol (OP)
(F)

Figure 1.24. Structure of several nonylphenols and octylphenol isomeres

The alkylphenols are mainly used to synthesize non-ionic surfactants (a surfactant or surfactant is a low molecular weight amphiphilic molecule, <1000 $g.mol^{-1}$.) The main surfactants produced by an etherification reaction are the alkylphenols-polyethoxylates (APEO) which have a hydrophobic part (chain of 6 to 20 carbons on average) and a hydrophilic part (COO- (-CH_2-CH_2-O-) (Figure 1.25). These compounds therefore have an essential characteristic: they are amphiphilic. Finally, the molecule comprises a variable number of ethoxylated group (-CH_2-CH_2-O-) (Lardy-Fontan 2008, *thesis unpublished*).

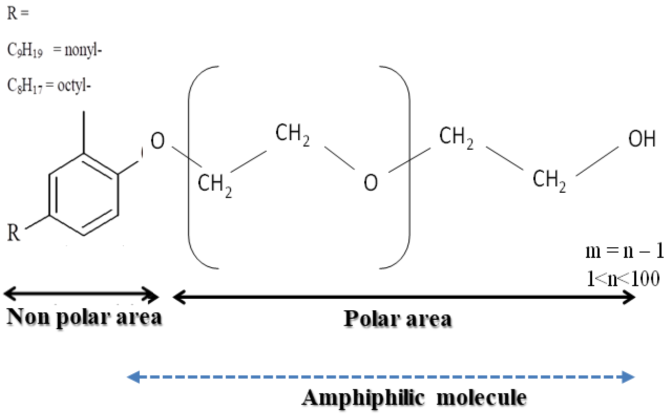


Figure 1.25. Molecule of alkylphenols polyethoxylates (Lardy Fontan 2008, *thesis unpublished*)

The most widely used APEOs are nonylphenol-polyethoxylated (NPEO) and octylphenol-polyethoxylated (OPEO) (80% and 20% respectively.) Worldwide production of APEO was estimated at about 500,000 tonnes for the year 1998, (according to ASPA, National Union of Manufacturers of Surface Agents and Industrial Auxiliary Products, the price of nonylphenol-polyethoxylated (NPEO) is € 1.2.kg^{-1} but varies with the purity of the product (INERIS 2005) The basic element of the molecule is a phenolic nucleus on which is substituted an alkyl radical.

1.5.2. Physico-Chemical Properties.

Table 1. 16. Physico-Chemical properties of 4-nonylphenol and octylphenol

No	Properties	4-nonylphenols	4-tert-octylphenols
1	Molecular Formula	$C_{15}H_{24}O$	$C_{14}H_{22}O$
2	Molecular Weight	220,3	206,3
3	Melting Point (°C)	81 - 83	84 - 85
4	Boiling Point (°C)	295 - 320	280 - 302
5	Color	Colorless to straw yellow (liquid)	White (solide)
6	Density	0,953	0,922
7	Vapor Pressure (Pa)	$(4{,}55 \pm 3{,}5).10^{-3}$	$4{,}7.10^{-3}$
8	Solubility (mg.l^{-1})	5,43	12,6
9	Log K_{ow}	4,2 – 4,48	4,12
10	Henry's Constant (Pa.m^3.mol^{-1})	11,02	0,70

According to the main characteristics in Table 1.16 allow these compounds accumulate in environmental matrices such as sediment, soil and sludge. Thanks to their half-life of 28 to 104 days, they are able to persist in several matrices (sediment, soil and water), (Maguire *et al* 1990). Nevertheless, on water surface NPs have half-life of 10 – 15 hours (Canada 2002). Furthermore, NPs and OP are much longer stable in the environment with a half-life of a few decades in the sediments either marine or fresh water ones (Isobe *et al* 2001; Duan *et al* 2014). Hence, NP and OP are ubiquitous in the general environment which many evidence presence their occurrence in sediments. (Isobe et al 2001 demonstrated that 20% of nonylphenols are found in the aquatic environment, in the particulate phase and 80% in the water itself. In the other side, suspended solids have a major role in the adsorption of these compounds in aquatic environments (INERIS, 2005).

Concerning risk assessment for these compounds, bioconcentration factor (BCF) of NP measured for fish was low, ranging from 87 to 344. However, the BCF for mussel ranges from 14 (low) to 3400 (moderate) (US - EPA 2010). Meanwhile Snyder et al 2001 revealed that fish exposed to 0.16 µg $NP.l^{-1}$ would assuming the BCF of 353 contain a concentration of 56.5 µg $NP.kg^{-1}$ which is only slightly less than the MDL 0.67 µg NP. kg^{-1}.

1.5.3. Use

Most of the alkylphenols are used as intermediates in the synthesis of derivatives which will have broad applications in areas ranging from surfactant formulations to pharmaceutical formulations. The main commercial outlets are nonionic surfactants, lubricant additives, phenolic resins, additives of different polymers, plasticizers and agrochemicals (Gong *et al* 2011). Among the various alkylphenols synthesized, one can enumerate, by grouping major compounds and large industrial applications (Lorenc *et al* 2003) :

1. 4-Nonylphenol. It is mainly used in the manufacture of a wide variety of surfactants but also in the synthesis of antioxidant compounds used in rubbers and other polymers, flame retardants and in the manufacture of thermal paper.
2. 4-tert-octylphenol. It is used in the manufacture of specialty surfactants, in the rubber industry (tackifier) and as an anti-UV stabilizer.
3. 4-dodecylphenol. It is mainly used in the manufacture of a wide variety of lubricating oil additives but also in specialty surfactants and as an emulsifying agent.
4. 4,4'-bis (2-sulfostyryl) biphenol (DSBP). It is mainly used in specialty surfactants and as wetting agent1 in agrochemicals.
5. Di-nonylphenol. It is used in the manufacture of specialty surfactants. The quantities produced remain limited. It was mainly used until the late 1960s as industrial detergents in the dyeing industry (Zoller and Sosis, 2009).

Production Rate

Annual NP production in Europe is in the order of 45.000 tonnes while it reaches 16.000 tonnes in China (Freenstra 2008). In Europe, production increased from 18.500 tons in 1984 to 4.900 tons in 1990 (INERIS 2005). In 1995, Germany had the consumption PA of 20.000 tons on which about 14.000 tons was nonylphenols. The remaining 6.000 tons were octylbutyl and other alkylphenols (Ahel *et al* 1994).

On the other hand, in the USA, the demand of AP dominated by p-nonylphenols of 105.000 tonnes/year followed by p-dodecylphenol of 87.000 $tonne.year^{-1}$. The least product demanded is DSBP and di-nonylphenol of 1000 and 1.500 tonne/year (Table 1.17). Similarly, the global demand is prominent by p-nonylphenol and p-dodecylphenol of 212.000 $tonne.year^{-1}$ and 137.000 $tonne.year^{-1}$ (Zoller and Sosis 2009).

Table 1.17. Worldwide and U.S. demand for APs (tonne.year^{-1})

No	Products	World demand	US demand
1	p-octylphenol	27.500	13.500
2	p-nonylphenol	212.500	105.000
3	p-dodecylphenol	137.500	87.500
4	DSBP (4,4'- Bis(2-sulfostyryl)biphenil	1000	1000
5	Di-nonylphenol	4500	1500

US = United State, APs = Alkylphenols

1.5.4. Sources, transport and fate of APs

Several European countries have established bans and restrictions on the application of these chemicals particularly NP and OP. Nevertheless, neither their production and import, nor the import of products containing these compounds is prohibited. Hence, it is plausible that these chemicals are encountered in many environmental matrices, even in food and human body as we mentioned earlier (Koniecko *et al* 2014; Staniszewska *et al* 2014/2015; Graca *et al* 2016).

NP and OP, as we are focusing in this recent work take part of the wide range compounds recognized as alkylphenols (APs). These compounds have been employed during several decades since they were produced. The particularly uses of NPs is for the synthesis of nonylphenol ethoxylates (NPEs). These chemicals are property to the world's third largest group of surfactants with numbers industrial, institutional and household employment. The OPs are also applied in the synthesis of octylphenol ethoxylates (OPEs). Nonetheless, its principal's use is the manufacture of phenolic resin, especially as a tackifier in the vulcanization for the production of rubber tires. It is well-known that the OP, NP and their ethoxylates are applied in textile industry, plastic manufacturing, water-based paints, herbicides, pharmaceuticals, cosmetics and washing agents, as well as in pulp and paper processing and steel manufacturing (Jahan *et al* 2008; COHIBA 2011a,b; Graca *et al* 2016).

Such the wide-ranging application induces NP and OP as widespread dissemination pollutants in natural environment mainly sediments, soil, and aerosols. The principal sources of these chemicals and their parent compounds (Ying *et al* 2002 ; Ahel *et al* 1994a,b) for the marine environment are municipal and industrial wastes. Several previous works revealed the atmospheric transport of APs (Moreau-Guigon and Chevreuil 2014 ; Salapasidou *et al* 2011 ; Ying *et al* 2006 ; Saito *et al* 2004 ; Dachs *et al* 1999).

Through the aerial medium, due to the hydrophobic nature of OP and NP, marine bottom sediments should be considered as a sink for these constituents. Anoxic regions of the sea bottom in particular are probably to deposit these substances since anoxic condition preserves OP and NP and favors formation of these constituents by decomposition of their ethoxylates (Ying *et al* 2002).

Accordingly, as we encountered in this work that APs transport originates from WWTPs discharges that flow out into the oceans. Some proportions of these compounds will slowly drift as the suspended materials and eventually deposited in the sediments. Meanwhile, some will undergo the evaporation due to solar radiation during summer season and float in the air. Since the influence of aerodynamic factors, these particles will be transferred from the air and re-deposited in the land area thanks to the aerodynamic processes. APs bound in the soil in high concentrations compared to other matrices (sediments and aerosols as previously reported (Cetin *et al* 2017; Lu *et al* 2016). It is also associated with buffering capacity, sorption to hydrophobic organic materials and stability of aggregate which are led to the high capacity of soil particles to bind organic compounds such as APs compared to other compartments such as sediments, waters and aerosols (Wershaw 1993).

1.5.5. The Alteration in the Environment

The decomposition of these chemicals in the environment can be via photodegradation or biodegradation one. In this work we have reviewed several articles which discussed the two processes of the alteration and the factors which play the essential role.

Photodegradation phenomena

The chemical compounds such APs will be decomposed through a processes named photolysis helped by the energy of sunlight. Research on this topic showed that for the decomposition of nonylphenols occurred at a light intensity of 0.05 to 0.09 $m^2.kW^{-1}h^{-1}$ (energy commensurate to summer noon) was essential (Ahel *et al* 1994). Additionally, these compounds were also photodegradable using visible light active carbon-doped TiO_2 (CDT) with anatase/rutile (A/R) ratio and immobilized on the surface of granular activated carbon (GAC) (Noorimotlagh *et al* 2018). It was suggested that the photolysis processes will gradually occur for etoxylated compounds compared to the alkylphenols (APs) ones and could take place barely in the surface layer of the water column and can be continued to the several centimeters (Ahel *et al* 1994).

NPs are able to be decomposed quickly in the waters where high oxygen condition due to photosensitization related to the abundance of dissolved organic matter (Ahel *et al* 1994). There were several physic chemical factors that play an essential role in terms of NPs photodegradation processes such as the availability of Fe^{3+} and reactive species of oxygen which are able to augment the kinetics of photodegradation. Inversely, dissolved organic matters appeared to decrease the kinetics of photodegradation. This photodegradation can produce the intermediate products such as 1,4-hydroxybenzene and 1,4-benzoquinone which do not appear to be estrogenic power.

The biodegradation phenomenon

Several in situ works of certain direct observations have been revealed in cultures, soils, sediments, wastewater and biosolids (Montgomery-Brown *et al* 2003; Priac *et al* 2017; Rajendran *et al* 2017; Bina *et al* 2018; Duan *et al* 2018).

Bai *et al* 2017 investigated that as an endocrine disrupter, most pure microorganisms can degrade only limited species of NP with low degradation efficiencies. To establish a microbial consortium that can effectively degrade different forms of NP, they isolated a facultative microbial consortium NP-M2 and characterized the biodegradation of NP by it. NP-M2 could degrade 75.61% and 89.75% of 1000 $mg.l^{-1}$ NP within 48 h and 8 days, respectively ; an efficiency higher than that of any other consortium or pure microorganism reported so far. The addition of yeast extract promoted the biodegradation more significantly than that of glucose. Moreover, surface-active compounds secreted into the extracellular environment were hypothesized to promote high-efficiency metabolism of NP.

The detoxification of NP by this consortium was determined. The degradation pathway was hypothesized to be initiated by oxidization of the benzene ring, followed by step-wise side-chain biodegradation. The bacterial composition of NP-M2 was determined using 16S rDNA library, and the consortium was found to mainly comprise members of the Sphingomonas, Pseudomonas, Alicycliphilus, and Acidovorax genera, with the former two accounting for 86.86% of the consortium. The high degradation efficiency of NP-M2 indicated that it could be a promising candidate for NP bioremediation in situ (Bai *et al* 2017).

The majority of NP isomers were degraded by 80% after 9 days of incubation (Gabriel *et al* 2008), inversely, several isomers were recalcitrant to degradation. For instance, approximately 30% of NP_{193} were removed. Nevertheless, thanks to the existence of a huge numbers of bacteria in the environment, biodegradation selectivity probably slower than that of in a pure culture. (Shan *et al* 2011) compared degradation of 5 synthetic NP isomers in a rice paddy soil under oxic conditions and the half lives followed the order: NP_{111} (10.3 d) > NP_{112} (8.4 d) > NP_{65} (5.8 d) > NP_{38} (2.1 d) > NP_{1} (1.4 d).

(Hao *et al* 2009) reported that biodegradation of NP was isomer selective in a sequencing batch reactor simulating the wastewater treatment process. Biodegradation of the 4 identified isomers followed the order: NP_{36} (75.4%) > NP_{111} (42.9%) > NP_{170} (40.7%) > NP_{194} (36.2%). The observed biodegradation rates were smaller than those reported by USEPA (2010). After examining 26 municipal wastewater treatment plants with full-scale activated sludge treatment, the range of NP removal was from 57% to 100% with an average of 90% (USEPA 2010). (Lu and Gan 2014b) investigated biodegradation of 18 NP isomers in two river sediments and found that biodegradation under oxic conditions was more efficient and demonstrated more significant isomer specificity. Under oxic conditions, the half lives ranged from 0.9 to 13.2 d while the values ranged from 15.6 to 20.1 d under slightly reduced conditions. The overall order of biodegradability of NP isomers in the oxic sediment was similar to that in incubation with S. xenophaga Bayram and also that in soil and bioreactor. Therefore, there may exist intrinsic properties influencing the biodegradability of NP isomers.

Additionally, the study findings suggested that technical nonylphenols (tNPs) are in fact a mixture of more than 100 isomers and congeners. Several recent studies showed that some of these isomers behaved significantly differently in occurrence, estrogenicity and biodegradability. The most estrogenic isomer was about 2 to 4 times more active than tNP. Moreover, the half lives of the most recalcitrant isomers were about 3 to 4 times as long as those of readily-biodegradable isomers. Negligence of NPs isomer specificity may result in inaccurate assessment of its ecological and health effects. The biodegradability of NP isomers with isolated bacterial strains and in soil, sediment and bioreactor showed a similar pattern: isomers with bulky α-substituents/shorter side chains exhibited longer half-lives or higher residues. Therefore, isomer specificity should be considered when evaluating the occurrence, fate, ecotoxicity and human health risks of NP.

Manzano *et al* (1999) have shown that the biodegradation of these compounds in river waters is profoundly affected by the temperature. Indeed, it conditions the acclimation of micro-organisms as well as the elimination rates the substances. Percentages of primary degradation range from 68% (at 7°C) to 96% (at 25 ° C); the percentages of mineralization, at 30 days, go from 30% (at 7°C) to 70% (at 25° C). Other authors (Fu *et al* 2007; Li *et al* 2008) have also concluded that seasonal may play an important role to this biodegradation. However, the accuracy of their conclusions must be considered with caution since most of these studies have been limited to two one-off sampling, therefore they did not take into account intrinsic variations in the systems (variations in inputs, intrinsic dynamics of the study system).

1.5.6. Toxicity

Recently, APs as the synthetic chemicals have been discovered disrupting and altering endocrine system of living organisms such as animals, plants and human beings despite at a low concentration ($ng.l^{-1}$) (Mijangos *et al* 2015; Luo *et al* 2017; Ismail *et al* 2018). The disturbance of endocrine system is induced by the ability of these compound to block and copy the usual effect of hormones, interrupt the synthesis and metabolism of hormones, and alter the hormone receptor levels (Hibberd *et al* 2009).

The contaminations of several environmental matrices such as sediment, soil and aerosol to APs are particularly derived from industrial and household discharges, land fill leachate, agriculture runoff, and wastewater and sewage treatment plant effluents (Pedersen and Lindholst 1999; Liu *et al* 2016; Ismail *et al* 2018).

The chemicals are transported to the water column will be adsorbed to the sediment, which induce to bioaccumulation and biomagnification through the food chain or the food web with humans as final consumer (Ismail *et al* 2017). Some aquatic animals such as crabs, shrimps and fish adsorb these APs via diffusion through gills and skin with a faster adsorption rate than that of other mediums (Luo *et al* 2017). At certain concentrations, this likely poses nuisances to the surrounding ecosystem; even the toxicities might be occurred. The toxicities of these compounds will decrease when the length of their ethoxylated chain increase. Therefore, APs are more toxic in the environment as they are the biodegradation products (Servos 1999). It is found as the evidences that LC_{50} of *Oryzias latipes* (killer fish) ranged between 1400 $\mu g.l^{-1}$ for NP to 11000 $\mu g.l^{-1}$ for $NP1_6EO$. Long-chain ethoxylated such as APEOs are considered as non-toxic, while. NPs are 200 times more toxic than NP_9EO (Servos 1999).

The two APs commercials that we are using in this work have similar acute toxicity values of 7 to 3000 $\mu g.l^{-1}$ in fish, 20 to 3000 $\mu g.l^{-1}$ in invertebrates, 27 to 2500 $\mu g.l^{-1}$ for algae (Servos, 1999). Furthermore, the toxicities of NP, NP_1E0, NP_2EO alone and in mixture (binary or ternary) on *Ceriodaphnia dubia* and *Pimephales promelas* were assessed and the results show that binary and ternary mixtures decrease the values of lethal concentrations (LC_{50}) in consequence of additive and synergistic effects (TenEyck and Markee2007). M eanwhile, the chronic toxicity values for octylphenol and nonylphenol are as low as 6 $\mu g.l^{-1}$ in fish, *Oncorhynchus mykiss* rainbow trout, NOEC (No Observable Effect Concentration) (in 91 days) and in the range of 3.9 $\mu g.l^{-1}$ for invertebrates, NOEL (No Observable Effect Level) in 28 days (Servos 1999).

According to the 4-NP toxicity data, it is widely accepted that an environmental background of 5 $\mu g.l^{-1}$ would be sufficient to put a significant proportion of aquatic communities at risk. The chronic toxicity values obtained in the toxicity tests have determined Predicted No Effect Concentrations (PNECs) in sediment and soil for certain alkylphenol compounds (INERIS 2014; European Council 2002), these values were used by Dong *et al* (2014) where PNEC for sediments is 39 $\mu g.kg^{-1}$ dw and soils is 300 $\mu g.kg^{-1}$ dw, respectively.

There were several works carried out to determine the values of LC_{50} showed the adverse effects to Pimephales promelas after 96 hours which were the concentrations of NP ranged between 128 to 300 $\mu g.l^{-1}$ (Holcombe *et al* 1984; Ward and Boeri 1991b; Brooke 1993; Naylor 1995; Weeks *et al* 1996). Similar to the results of 18 different species of fish ranged between 100 to 300 $\mu g.l^{-1}$. However, it was found in higher concentrations of these compounds for LC_{50} of 190 to 920 $\mu g.l^{-1}$ in trout rainbow Brooke 1993; Dwyer *et al* 1995; Naylor 1995).

It is more sensitive, concerning the reproduction and growth of *Ceriodaphnia dubia* the LC_{50} will achieve at the concentration of 69 µg.l^{-1} after 96 hours (Weeks *et al* 1996). For the mysis *Mysidopsis bahia*, the CSEO (on the growth) was of 3,9 µg.l^{-1} (Ward and Boeri, 1991c). (Ankley *et al* 1990; Brooke 1993; Comber *et al* 1993; Naylor 1995) investigated for *Daphnia magna* and found the values of LC_{50} after 48 hours with magnitude of the concentrations of 93 to 470 µg.l^{-1}. Concerning the reproduction, this species will undergo a nuisance effect when the concentration level of this compound reaches 24 µg.l^{-1} after 21 days.

Macrobenthos such as amphipoda in fresh water *Hyalella azteca* will be have an adverse effect after 96 hours within the concentrations of NP of 20 µg.l^{-1} (Brook 1993). Concerning the plants, the photosynthetic activities and the growth will be declined within the condition of NP concentration between 125 to 500 µg.l^{-1}. On the other hand, there was no effect on zooplankton in NP concentrations of 5 µg.l^{-1} in water (O'Halloran *et al* 1998). Schmud *et al* 1998 suggested that the abundance of some macro-invertebrates will be reduced significantly up to 100% when the concentration of these compounds exceed 243 µg.l^{-1}.

According to ecotoxicological properties of APs, compounds typically used in cleaning products are in a comparable range. Acute aquatic toxicity to fish, daphniae and algae is generally between 1 and 10 mg.l^{-1} (LC/EC_{50}), but algal toxicity often seems to be the most sensitive endpoint also implying EC_{50} values in the range of 0.1–1 mg.l^{-1}. The bacterial toxicity is generally very low so that it can be concluded that inhibitory effects by non-ionic surfactants to the bacterial biocenosis in WWTP are rather improbable. The long-term toxicity NOEC values support the general rule that they are around one order of magnitude lower than the acute EC/LC_{50} values. It should be noted that the aquatic toxicity of non-ionic surfactants follows certain general rules. The toxicity increases with increasing alkyl chain length and hydrophobicity of the molecule, while the influence of the poly(ethoxylate) chain length is not very pronounced except for long-chain ethoxylates exhibiting a significantly reduced ecotoxicity.

Furthermore, LC_{50} for chronic OP exposure during 8 weeks was 29±6 µg.l^{-1} to sand goby (*Pomatocchistus minutus*) in the estuarine of Glasgow, UK (Robinson *et al* 2004). In the meantime, these APs can cause the chronic effect (EC_{50}) for *Ceriodaphnia dubia* for 48h and *Daphnia magna* for 24 h. These concentrations chronic were 0,008 to 0,47 mg.l^{-1} and 0,00093 to 0,7 mg.l^{-1}, respectively.

1.5.7. The concentration estimation of APs in sediments throughout the world during the last three decades

Table 1.18 allows us to assess the level of APs contaminations in the sediments around the globe. In the period of 1990 to 1999, we have a high contamination of APs especially NPs of 370 mg.kg^{-1} in Santa Monica Basin, Southern California, (USA) which was likely the highest polluted induced by these emerging pollutants approximately during three last decades. This magnitude of NPs concentrations linked to the effluent sludge which is classified as the chronicle pollution (Chalaux *et al* 1992). During this era, the least concentrations levels were found in St Laurence River, USA (Bennie *et al* 1997) which was directly connected to Industrial area and WWTPs. Subsequently, the next decade, we recorded the concentration of these chemicals were ranged between 0.1 µg.kg^{-1} to 194 mg.kg^{-1}. The most elevated contaminant was encountered in Ter River Catalonia, NE Spain where was related with the Sludge of WWTPs. The last decade, we have found the important NPEOs contaminations of 234 mg.kg^{-1} and NP and of 93 mg.kg^{-1} in Heraklion WWTPs, Greece (Chokwe *et al* 2015).

As summarized in Table 1.18, we noticed that several places in the world are heavy contaminated by these substances. Additionally, all information on the pollution in the world related these emerging pollutants are the area exposed to the significant anthropogenic inputs and directly linked with the sludge.

Table 1.18. The Occurrence of OPs, NPs, OPEO and NPEO in sediments throughout the world (1990 to 2017)

Sources	Concentrations	Locations	References
Connected with WWTPs	NP (500 – 4700 µg.kg^{-1})	Venice Lagoon, Italy	Marcomini *et al* (1990)
Effluent Sludge	NP (370.000 µg.kg^{-1})	Santa Monica Basin, Southern California	Chalaux *et al* (1992)
Industrial area, connected to WWTPs	4-t-OP (< 10 – 1800 µg.kg^{-1}) NP_1EO (< 15 – 38000 µg.kg^{-1}) NP_2EO (< 15 – 6000 µg.kg^{-1})	St Laurence River, USA	Bennie *et al* (1997)
Connected to Off shore oil platform	NP (1000 – 15000 µg.kg^{-1})	Estuarine, UK	Blackburn *et al* (1999)
Recycle paper Sludge	4NP (2350 – 4610 µg.kg^{-1}) 4-t-OP (50 – 180 µg.kg^{-1}) NP_1EO (70 – 210 µg.kg^{-1}) NP_2EO (80 – 390 µg.kg^{-1})	Canada	Hawrelak *et al* (1999)
Possible estrogenic impacts	OP (21 – 116 µg.kg^{-1}) NP (367 – 1029 µg.kg^{-1})	North Sea	Heemken *et al* (2001)
Connected to WWTPs	NP (2000 – 15300 µg.kg^{-1})	Kalamazoo River, Michigan	Kannan *et al* (2003)
Domestic and tourism activities	NP (10.4 – 5054 µg.kg^{-1})	Shiwa Lake, Korea	Li *et al* (2004)
Connected to Sewage	4-t-OP (2 – 12 µg.kg^{-1}) 4 NP (4 – 5 µg.kg^{-1})	River Ouse, East Sussex, UK	Liu *et al* (2004)
Developing regions and high urbanized	OP (1 - 18 µg.kg^{-1}) NP (60 - 571 µg.kg^{-1})	Pearl River Estuary, China	Chen *et al* (2005)
Commercial harbor and shipping yards	OP (4.61 µg.kg^{-1}) NP (89.1 µg.kg^{-1})	Yeongil Bay, Korea	Koh *et al* (2006)
Connected to STPs	NP (37 - 664 µg.kg^{-1})	South China Sea	Peng *et al* (2007)
Suburb, Farm lands, agriculture area	4-t-OP 0,1 – 8,6 µg.kg^{-1}) 4NP (0,1 – 3,1 µg.kg^{-1})	Sao Paulo, Brazil	Fiedler *et al* (2007)
Possible estrogenic impacts	NP (2700 µg.kg^{-1})	Tokyo Bay, Japan	Kurihara *et al* (2007)
Sludge, Connected to WWTPs	NP (194 mg.kg^{-1})	Ter River Catalonia, NE Spain	Cespedes *et al* (2008)
Connected to WWTPs	OP (< 0.2 – 11 µg.kg^{-1}) NP (<0.2 – 34 µg.kg^{-1})	Estuarine Savannah, GA, USA	Kumar *et al* (2008)
Sedimentation caused by dam construction	4-t-OP (nd – 3.0 µg.kg^{-1}) 4NP (nd - 64 µg.kg^{-1})	Estuarine of Nagara River, Japan	Funakoshi and Kasuya (2009)
Urban, industrial and agricultural activities	NP (5999 µg.kg^{-1})	Ebro River Basin, Spain	Navaro-Ortega *et al* (2010)
Connected with WWTPs	OP (15.1 – 31.1 µg.kg^{-1}) NP (145 – 349 µg.kg^{-1})	Henan Province, China	Zhang *et al* (2011)
Connected to WWTPs	4-t-OP (<0.2 210 µg.kg^{-1}) 4NP (107 – 16198 µg.kg^{-1})	Pearl River Delta, China	Gong *et al* (2011a)
High urbanized and industries	OP (<1 - 463 µg.kg^{-1}) NP (31 – 31885 µg.kg^{-1})	China	Gong *et al* (2011b)
Connected to WWTPs	NP(22 - 86 µg.kg^{-1}) NP_1EO (<1 - 40 µg.kg^{-1})	Urban Estuary, Greece	Klosterhause *et al* (2013)

Connected to sewage outfall	OP (5 -22 µg.kg^{-1}) NP (124 – 4843 µg.kg^{-1})	Seawage holding Lake, China	Jin *et al* (2013)
Connected to WWTPs	4-t-OP (<100 – 135 µg.kg^{-1})) 4NP (<100 - 32000 µg.kg^{-1}) NPEO (<100 – 1600 µg.kg^{-1}))	Estuarine, Auckland, New Zealand	Stewart *et al* (2014)
Urban and high industries area	OP 0.7 – 11.1 µg.kg^{-1}) NP (31.3 – 1642.8 µg.kg^{-1})	Yellow Sea and East China Sea	Duan *et al* (2014)
High industries and connected to WWTPs	OP (nd - 76 µg.kg^{-1}) NP (nd - 1693 µg.kg^{-1}) OP$_1$EO (nd – 0.23 µg.kg^{-1}) NP$_1$EO (nd – 119 µg.kg^{-1})	Iberian River, Spain	Gorga *et al* (2015)
Sludge	NP (93 mg.kg^{-1}) NPEO (234 mg.kg^{-1})	Heraklion WWTPs, Greece	Chokwe *et al* (2015)
Domestic, agricultural and nautical activities	4-t-OP (9.3 µg.kg^{-1}) NP (74.5 µg.kg^{-1})	European River Basin, Portugal	Salgiero-Gonzales *et al* (2015)
Connected to WWTPs	OP (38.18 µg.kg^{-1}) NP (20.66 µg.kg^{-1})	Taihu Lake and its Tributeries, China	Liu *et al* (2016)
Possible estrogenic impacts	∑AP (95 – 130 µg.kg^{-1})	West Coast of South Africa	Jeon *et al* (2017)
Industrial and domestic area, International trade port	AP (9.46 µg.kg^{-1})	Geum River Estuary, Korea	Yoon *et al* (2017)

WWTPs = Wastewater treatment plants, APs = Alkylphenols, NPs = Nonylphenols, OP = Octylphenols, NPEO = Nonylphenol polyethoxylates, OPEO = Octylphenol polyethoxylates, STPs = Sewage treatment plants

1.5.8. Review of Analytical Methods

The nuisance of APs in the environment, particularly in the aquatic area, has become a public concern in several recent decades due to their widespread existence in the various environmental matrices and their capacity interfering with hormonal systems. They pose their toxicological effects at very low concentrations and their widespread usage in industrial and household applications induce the risks not only for living organisms but also for public safety. APs are well-detected as low as part per billion (ppb) and part per trillion (ppt) particularly in the aquatic area as we mentioned earlier. These low-level records of APs concentrations in the sediments are likely particularly because of advancements in sample preparation and instrumental techniques that continue to evolve rapidly. Therefore, the development of the analytical methods to assess these chemicals at trace levels in the sediment matric is urgently required. This review discusses the trends in analytical methods for APs in sediment during at least the last three decades (Table 1.19).

The description on extraction, purification and analytical identification is described in detail, including the quality assurances and the recoveries of each method that were developed. The first decade of 1990 to 1999 people extracted APs in the sediment samples using various devices such as soxhlet apparatus, ultra sonication, and others to separate these compounds. Meanwhile, glass column chromatography with silica gel was the best choice to clean up the extracts. Several works commenced the analysis using GC/MS to identify these substances in the sediments (Marcomini *et al* 1990; Chalaux *et al* 1992; Bennie *et al* 1997; Blackburn *et al* 1999; Hawrelak *et al* 1999). The good recovery results ranged between 76 to 97% which were categorized as feasible methods. Concerning the decade of 2001 to 2010, despite of time and solvents consuming people still used soxhlet apparatus along with ASE which was more efficient. Some used ultra-sonication which has no significant differences in term of the recoveries. The fractionations using glass column chromatography were the predominantly preference along with SPE. Unlike the last period, most of the works employed GC/MS as the more sophisticated devices after having had the derivatization of BSTFA/TMCS (Heemken *et al* 2001; Kannan *et al* 2003; Liu *et al* 2004; Li *et al* 2004; Chen *et al* 2005; Koh *et al* 2006; Fiedler *et al* 2007; Kurihara *et al* 2007 Peng *et al* 2007; Cespedes *et al* 2008 Kumar *et al* 2008; Funakoshi and Kasuya 2009; Navaro-Ortega *et al* 2010). We observed that there is no significance different of the methods development during three decades. This is because recent decades, investigators returned to the ultra-sonication extraction along with soxhlet apparatus, while the purification still used the layers of silica gels with glass column (Gong *et al* 2011a,b; Zhang *et al* 2011; Jin *et al* 2013; Klosterhause *et al* 2013; Duan *et al* 2014; Stewart *et al* 2014; Chokwe *et al* 2015; Liu *et al* 2016; Jeon *et al* 2017; Yoon *et al* 2017). Nevertheless, people commenced to employ the most sophisticated devices to identify these APs by using LC/MS/MS with the excellent performance (Gorga *et al* 2015; Salgiero-Gonzales *et al* 2015).

Tabel 1.19. Review of analytical method (1990 to 2017)

Extraction	Purification	Identification	Performance	References
Soxhlet (n-hexane)	Minicolumn cartridge rinsed with hexane, amino silica cartridge performed by acetone	LC – Fluorescence Spectrophotometer	Recoveries 84 – 97%	Marcomini *et al* (1990)
Virtis homogenizer (MeOH/DCM)	Silica alumina column, elution with DCM	Derivatisation BSTFA prior to Capillary GC	LOD 2 ng.g^{-1}	Chalaux *et al* (1992)
Soxhlet with DCM	Silica gel column, elution with methanol in DCM	GC/MS	Recovery 80%	Bennie *et al* (1997)
Acetylated centrifuge (DCM)	HPLC clean up with Silica gel column	Derivatisation BSTFA prior to GC/MS identification	LOD = 0.001 – 0.1 µg.g^{-1}	Hawrelak *et al* (1999)
Ultrasonication with ethyl acetate	C18 SPE column elution with ethyl acetate and DCM	GC/MS	Recoveries 76 – 80%	Blackburn *et al* (1999)
ASE n-hexane/acetone	HPLC clean up (hexane/DCM)	Derivatisation with heptafluorobutyric acid anhydride prior to GC/MSD		Heemken *et al* (2001)
Steam distillation	Silica column by isocratic, elution with MeOH/DCM/n-hexane	HPLC with FD, confirmed with GC/MSD with SIM	Recovery >70%	Kannan *et al* (2003)
Mechanical shaker (DCM)	Column fractionation	Derivatisation BSTFA, GC/MS		Li *et al* (2004)
MAE	Silica gel column, elution with acetae-hexane	Derivatisation BSTFA/TMCS prior to GC/MS	Recoveries 61 – 133%	Liu *et al* (2004)
Soxhlet (DCM) solvent exchanged to n-hexane	Silica gel column, elution with DCM/n-hexane	GC/MS	Recoveries 87 – 106%	Chen *et al* (2005)
Soxhlet (DCM)	Column fractionation with silica gel, elution with n-hexane and DCM	GC/MSD		Koh *et al* (2006)
Ultrasonic extraction	Silica column with 3 steps of isocratic elution	BSTFA derivatisation prior	Recovery 83%	Kurihara *et al* (2007)

(DCM)		to GC/MS		
ASE	Silica gel column conditioned with hexane and elution with DCM/hexane	BSTFA derivatisation prior to GC/MS	Recoveries 84 – 97%	Fiedler *et al* (2007)
Sonication (Acetone/DCM), transferred into the funnel contained saturated NaCl solution		GC/MS	Recoveries 79 – 86%	Peng *et al* (2007)
ASE, acetone/methanol	SPE Li Chlorut C18 cartridge	HPLC-MS	Recoveries 47 – 113%, LOD (5 – 23 µg.kg^{-1})	Cespedes *et al* (2008)
Soxhlet extraction (DCM)	Florisil glass column, elution with DCM in Methanol	HPLC with fluorescence detection	Recoveries 90 – 105%	Kumar *et al* (2008)
Ultrasonic vibration with acetone	Silica gel column elution with n-hexane/acetone	Trimethyl Sylilation prior to GC/MS	Recoveries 89 - 103%	Funakoshi and Kasuya (2009)
ASE, Hexane/DCM	Florisil column, elution with n-hexane/DCM	GC/MS	Recovery 60%	Navaro-Ortega *et al* (2010)
Ultrasonic (Acetone/MeOH)	Florisil column, elution with hexane, hexane/DCM and ethyl acetate	GC/MS		Zhang *et al* (2011)
Ultrasonication with methanol and acetone	Silica gel column conditioned with ethyl acetate/hexane and elution with ethyl acetate/hexane	Derivatisation MSTFA prior to GC/MS	Recoveries 85 - 125%	Gong *et al* (2011a)
Soxhlet with DCM exchanged to n-hexane	Silica gel column, elution with DCM hexane	Derivatisation MSTFA prior to GC/MS	Recoveries 85 - 101%	Gong *et al* (2011b)
Soxhlet extraction (Acetonitrile)	Silica column elution with actetae/n-hexane	Derivatisation MSTFA prior to GC/MS	Recoveries 85 – 106% LOD (0,2 – 1,5 ng.g-1)	Jin *et al* (2013)
Digested in methanolic KOH extracted with hexane and acetylated by treatment with anhydride and pyridine	Silica column chromato	GC/MS		Klosterhause *et al* (2013)
Ulrasonic extraction with hexane and acetone	Multilayer Silica alumina, elution with DCM/hexane	GC/FID	Recoveries 92 – 104%	Duan *et al* (2014)
		GC/MS	Recoveries 68 – 116%	Stewart *et al* (2014)
PLE, re-dissolved in methanol		TFC-LC-MS/MS		Gorga *et al* (2015)
Centrifuge with hexane/acetone	Silica gel column, elution with DCM	Derivatisation TEA and HFBA prior to GC/MS	Recoveries 62 – 106%	Chokwe *et al* (2015)
SPME	Alumina and C18 reconstituted with methanol	LC MS/MS	Recoveries 84 – 103%	Salgiero-Gonzales *et al* (2015)

Ultrasonic extraction, hexane/DCM	SPE	HPLC-MS/MS		Liu *et al* (2016)
Soxhlet with DCM, replaced with n-hexane	Silica gel, elution with DCM/hexane	GC/MS	Recoveries 75% MDL 0,09 – 0,97 ng.g^{-1}	Yoon *et al* (2017)
Soxhlet (DCM)	Column fractionation with silica gel, elution with n-hexane	GC/MS	Recoveries 74 – 112 %	Jeon *et al* (2017)

GC/MS = gas chromatography/mass spectrometry, DCM = dichloromethane, SPE = solid phase extraction, SPME = solid phase micro-extraction, TEA = triethylamine, LC MS/MS = liquid chromatography mass spectrometry/mass spectrometry (tandem mass), HFBA = heptafluorobutyric anhydride, TFC-LC-MS/MS = Turbulent-flow chromatography-liquid chromatography-mass spectrometry/mass spectrometry (tandem mass), MSTFA = N-Trimethylsilyl-N-methyl trifluoroacetamide, BSTFA/TMCS = N,O-Bis(trimethylsilyl)trifluoroacetamide/Trimethylchlorosilane, GC/FID = gas chromatography/flame ionization detector, HPLC = high performance liquid chromatography.

CHAPTER II

MATERIALS AND METHODS

2.1. Description of Study Site

The inshore of South East France and Var departments in France are well-known for their rich multifariousness and environmental essence (Abucaya *et al* 2001). This biogeographical area is part of ten biodiversity with a place of significant activities in the Mediterranean Basin (Medail and Quezel 1997). So as to better mitigate, protect and conserve against anthropogenic impacts, 'Calanque National Park'has been established in 2012. This region located in Southern France which extends over 520 km^2 of which 85 km^2 is land, while the remining is marine area. This is the the first suburban nationa park in Europe. It includes parts of the Massif of Calanque stretching between Marseilles and Cassis. We have chosen our study site at center of the Calanque National Park encompasses the Friou archipelago, plane, the Marseilleveyre Islands and Cap Croisette up to Green Island where the potential pollutants of the marine environment particularly derived from treated urban wastewater discharged at a rate of up to 280,000 m^3 each day. This includes used water from Marseilles and its suburbs, a population of at least 1.8 million people. Other potential persistent organic pollutants (POPs) derived from Marseilles and the Huveaune River, particularly during intense rainfall, can be by passed through the Cortiou messenger. In 2008, Marseilles authorities upgraded their wastewater treatment plan 'Géolide' by integrating a biological treatment which considerably reduce the impact of urban organic pollutants on the marine environment but did not entirely resolve the problem of some POPs such as Polycyclic Aromatic Hydrocarbons (PAHs) that have been identified in previous studies (Mille *et al* 2007; Asia *et al* 2009). However, to the best our knowledge, there are no published data for Linear Alkylbenzene (LABs), Organochlorine Pesticides (OCPs), Polychlorinated Bephenyls (PCBs) and Alkylphenols (APs)(the previous study was (Lardy-Fontain 2012, *thesis unpublished*).

This study was undertaken within the framework of the French National Research Agency (ANR) program MARSECO. We investigated the extent of PAHs, OCPs, PCBs and APs in the sediments and their potential recent contamination through indices of pollution and potential environmental risk as well as their temporal trends.

2.2. Sample Collection

As shown in Fig. 2.1 and table 2.1, samples from 12 stations (three independent subsamples per station) were collected from sewage outfall of the wastewater treatment plant of Cortiou – Marseille, France. Surface sediment samples were collected on 21st March and 23rd June 2010 with a sediment grab sampler (Shiptex ; Wildco, USA) and PVC core samplers (Ø 100 mm) using SCUBA equipment. The sampling points lie perpendicularly to the coast line (237ºN) starting from the sewer outlet to the seaward. All sediments samples were freeze-dried, then sieved using a 2 mm mesh size, homogenized and stored at -18ºC prior to analysis.

Table 2.1. Geographic position of sampling stations

Sediment stations	**Coordinate positions**	
	Longitude	**Latitude**
P1	43°12'44.58"N	5°24'11.28"E
P2	43°12'43.38"N	5°24'11.04"E
P3	43°12'40.56"N	5°24'11.46"E
P4	43°12'39.66"N	5°24'12.18"E
P5	43°12'37.80"N	5°24'12.66"E
P6	43°12'33.66"N	5°24'14.64"E
P7	43°12'27.36"N	5°24'14.16"E
P8	43°12'25.98"N	5°24'14.76"E
P9	43°12'21.96"N	5°24'14.64"E
P10	43°12'30.27"N	5°24'10.29"E
P11	43°12'29.93"N	5°24'18.11"E
P12	43°12'34.69"N	5°24'8.47"E
Soil Stations	**Longitude**	**Latitude**
S1	43°1'51.46"N	5°24'8.66"E
S2	43°12'53.97"N	5°24'3.67"E
S3	43°12'56.63"N	5°23'59.49"E
S4	43°13'1.92"N	5°23'55.67"E
S5	43°12'55.13"N	5°24'9.18"E
S6	43°12'53.97"N	5°24'12.64"E
Aerosol Station	43°13’21.96” N	5°21’4.55” E

2.3. Laboratory Analysis

2.3.1. Hydrocarbon and Linear Alkylbenzene

Chemicals

Supra Solv grade (Merck, Darmstadt, Germany) solvents such as acetone (AC), dichloromethane (DCM) and nhexane (HEX) were purchased from VWR International (Fontenay Sous Bois, France). Acetonitrile of high-performance liquid chromatograph (HPLC) grade (Merck) and water purified with a Milli-Q system (Millipore, Bedford, MA, USA) were used throughout the liquid chromatography analysis.

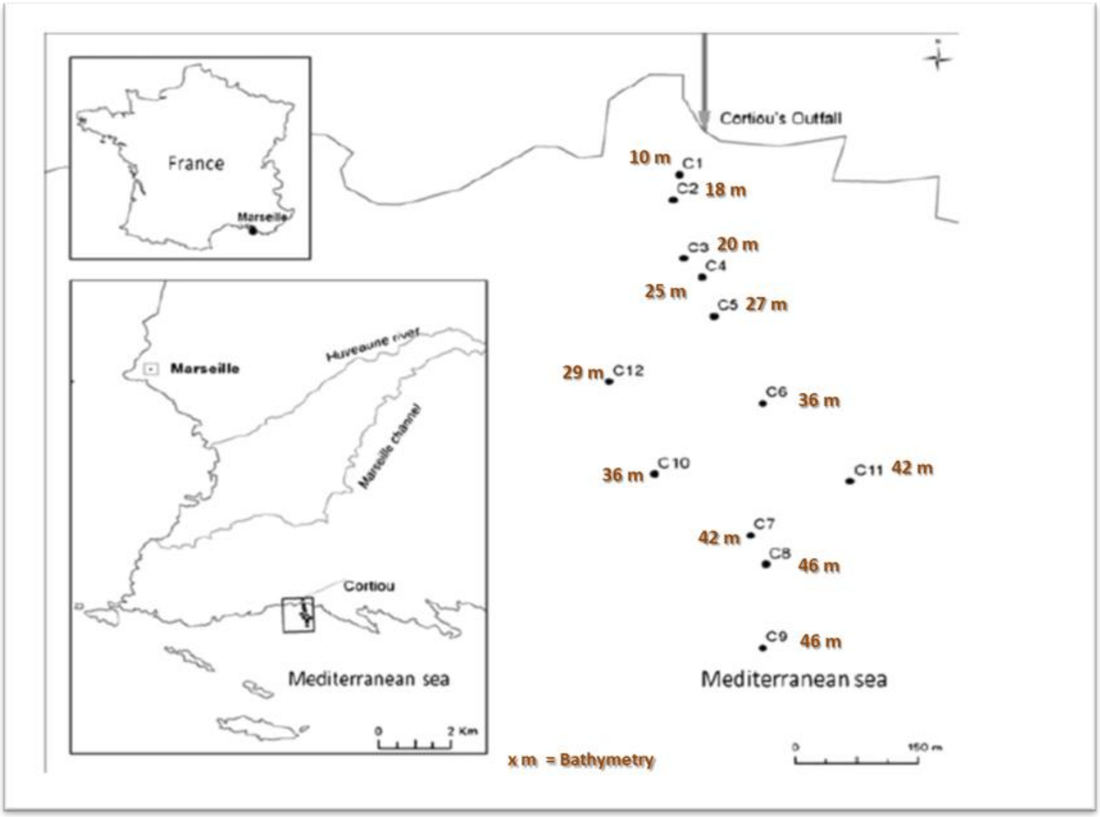


Figure 2.1. Study site

The reference standard mixture containing 16 US EPA priority PAHs, namely naphthalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo(a)anthracene (B[a]Ant), chrysene (Chr), benzo(b)fluoranthene (B[b]Fl), benzo(k)fluoranthene (B[k]Fl), benzo(a)pyrene (B[a]Pyr), indeno (1,2,3-cd) pyrene (Ind), dibenzo(a,h)anthracene (dB[ah]Ant) and benzo(ghi) perylene (B[ghi]P), at concentration levels between 100 and 2,000 mg ml^{-1} in methanol/dichloromethane (1:1; v–v) was obtained from Supelco (Bellefonte, PA, USA). Labeled n-alkane (n-nonadecane-d$_{40}$) and 1-phenylnonane were purchased from Sigma-Aldrich, St. Louis, MO, USA. Standard working solutions were diluted by DCM. A standard certified reference material (harbor marine sediment HS-5) was obtained from Laboratory of the Government Chemist (LGC) Promochem.

Fontainebleau sand was provided by Carlo Erba reagents (Milan, Italy). Alumina, silica-gel 60 (200–300 mesh) and anhydrous sodium sulfate (Na_2SO_4) were purchased from VWR International. The alumina and silica-gel, silica was deactivated with 5 % water (w:w), and Na_2SO_4 was baked for 48 h at 550ºC before use. Analytical reagent grade of glucose and H_3PO_4 were purchased from Fisher Scientific. $NaHCO_3/Na_2CO_3$ was supplied from Shimadzu.

Sample extraction and analysis

The sample extraction and analysis were conducted according to Kanzari *et al* (2012) and Syakti *et al* (2013). Briefly, 10 g of freeze-dried sediments was transferred to a precleaned cellulose extraction thimble and extracted using a Soxhlet extractor apparatus for 16 h with a 200 ml mixture of DCM and

HEX (1:1, v/v). Prior to extraction, nonadecane-d_{40} was added to the samples as an internal standard (IS) for n-alkane quantification. All or part of the extractable organic matter (EOM), depending on the initial weight, was dissolved in n-hexane and applied to a 50 % alumina 50 % silica (8 g of each, both deactivated with 5 % H_2O) chromatography column (30 9 1 cm). The saturated fraction (F1) was first eluted with 30 mL of HEX. Elution with 20 ml of HEX/DCM (9:1) and 40 mL of HEX/DCM (4:1) was combined to yield the aromatic fraction (F2). Sulfur interference was removed by shaking the extract with copper powder previously reduced with diluted hydrochloric acid (0.1 M) (Blumer 1957). A labeled n-alkane (n-nonadecane-d_{40}) was added to each sample and the matrix blank prior to extraction as surrogate to assess the overall procedural recovery. In this study, n-alkane surrogate recoveries were 98 to 102 %. Concerning PAHs, an HS-5 certified sediment was analyzed to evaluate the extraction accuracy. Reproducibility estimated for PAHs on triplicate samples was >90 %. Each fraction was evaporated on a rotary evaporator and under a gentle stream of nitrogen, and the dry residue was weighed (microbalance, Perkin–Elmer AD2Z). The sum of the aliphatic and the aromatic fractions gave the total hydrocarbon content (THC). F1 was diluted in HEX, and the nalkanes present were separated by capillary gas chromatography (GC) under the following equipment: GC Autosystem XL Perkin Elmer chromatograph with on-column injection and a Perkin Elmer Elite-XLB column (30 m 9 0.25 mm ID 9 0.25 lm film thickness). Helium was used as the carrier gas at a constant rate of 1 mL min^{-1}. The temperature was programmed from 70 to 285ºC (5ºC min^{-1}) and then held for 30 min. The mass spectrometer was operated in the electron impact ionization (EI) mode (70 eV) and simultaneously scanned in both Full Scan and Selected Ion Monitoring (SIM) modes. LAB identification relied on both retention times and characteristic ions. The 91 m/z ion was used for quantification, and the 105 and 119 m/z ions were used for confirmation with 1-phenylnonane as internal standard. Conventionally, these isomers are described using the form n-Cm-LAB, where n = the position of the benzene ring and m = the number of carbon atoms in the aliphatic chain. Aromatic hydrocarbons (PAHs) contained in F2 were analyzed using a Prostar (Varian, Palo Alto, CA, USA) HPLC equipped with a thermally controlled autosampler and a programmable fluorescence detector (HPLC–PFD). Excitation/emission time windows for the fluorescence detector are described in Fig. 2.2 The injection vial and the analytical column were maintained at 10 and 35ºC, respectively, for all analyses. The separations were carried out using a reverse-phase C_{18} column (250 mm x 4.6 mm x 5 µm, ChromSpher 5PAH, Varian) protected by a C_{18} guard column (10 mm 9 3 mm, 5 mm, Chromguard). Aliquots of 20 µl were injected, and the flow rate was held at 1.2 ml. min^{-1} for a total run time of 55 min. The data were acquired and processed using the Galaxie^{TM} software package (Varian).

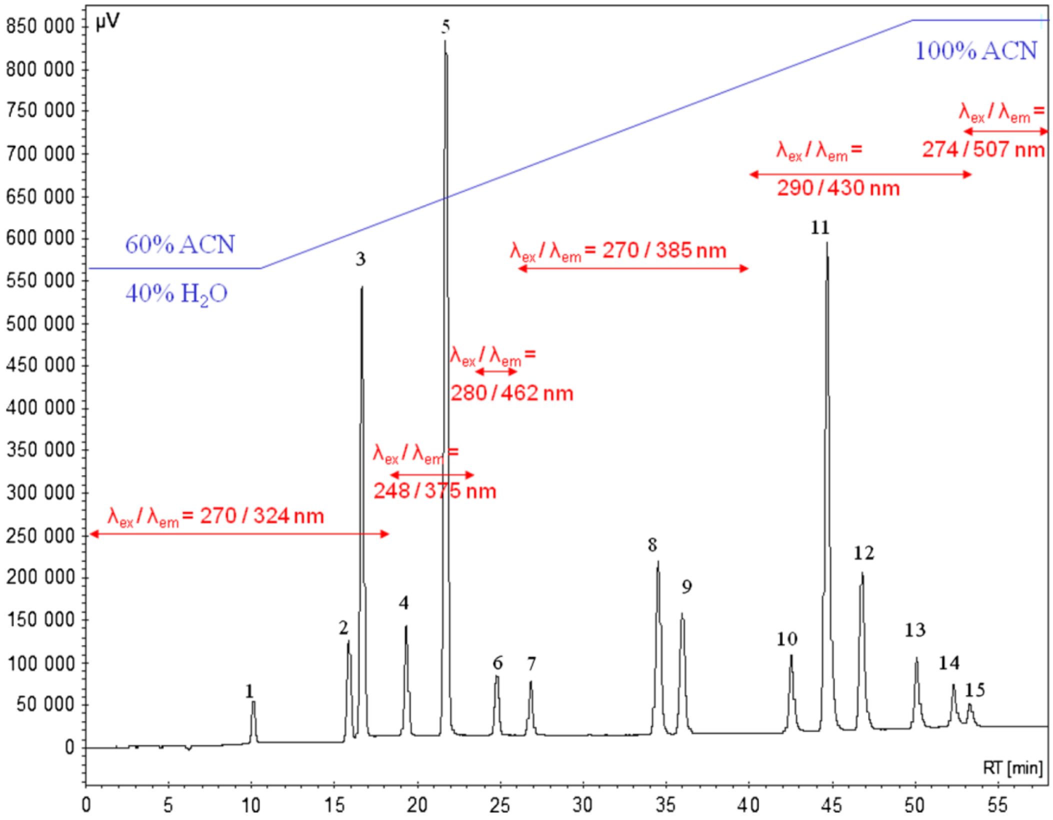


Figure. 2.2. HPLC–PFD chromatogram obtained from Cortiou sediments. Peak identities are (1) naphthalene (Na), (2) acenaphthene (Ace), (3) fluorene (F), (4) phenanthrene (Phe), (5) anthracene (Ant), (6) fluoranthene (Fl), (7) pyrene (Pyr), (8) Benzo(a)anthracene (B[a]Ant), (9) chrysene (Chr), (10) benzo(b)fluoranthene (B[b]Fl), (11) benzo(k)fluoranthene (B[k]Fl), (12) benzo(a)pyrene (B[a]Pyr), (13) indeno (1,2,3-cd) pyrene (Ind), (14) dibenzo(a,h)anthracene (dB[ah] Ant) and (15) benzo(ghi) perylene (B[ghi]P). The excitation (kex) and emission (keM) wavelength program to determine individual PAHs and gradient elution program using solvent with fluorescence detection following liquid–liquid A (Acetonitrile) and solvent B (water).

The total carbon (TC) content was determined using the high-temperature (900ºC) catalytic oxidation method with IR detection of CO_2 (Benner and Strom 1993). The inorganic carbon content was determined after addition of H_3PO_4 at 200ºC followed by IR quantification of CO_2, calibrated using $NaHCO_3/Na_2CO_3$. The total organic carbon (TOC) content was calculated by subtracting the TC content from the inorganic carbon content. All data in this work concerning contaminants concentrations in sediment (μg.kg^{-1}) were expressed related to dry weight sediment.

Statistical analysis

The analysis of variance (ANOVA) and linear regression were employed to compare differences in Σ n-alkane, ΣPAHs and ΣLABs with the physicochemical properties (EOM, TC and TOC) in the surface sediments of Cortiou and to explore correlations between these parameters. A *p* value of 0.05 or less was regarded as being significant for all the tests. The statistical analyses were implemented using the SigmaPlot for Windows$^{®}$ version 11.0 (Systat Software, Inc., wpcubed, GmbH, Germany).

2.3.2. Organochlorine Pesticides and Polyclhorinated Biphenyl

Chemicals

Organochlorine pesticides (OCs) and some related metabolites, such as aldrin, α-, β-, δ-, γ-HCH, dieldrin, α-endosulfan, β-endosulfan, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, methoxychlor, p,p'- dichlorodiphenyldichloroethane (p,p'- DDD), p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), were purchased from Supelco at 2.000 µg ml-1 in toluene:hexane (50:50/v:v). PCBs (congeners 28, 52, 101, 118, 138, 153,180) were purchased in the form of 10 ng μg^{-1} in iso-octane solution from Dr. Ehrenstorfer (Augsburg, Germany). Mirex PESTANAL was purchased from Sigma-Aldrich (St. Louis, MO, USA). IUPAC nomenclature of mentioned compounds is in Electronic Supplementary Material (Text 1). Standard working solutions were diluted with dichloromethane (DCM) (SGS, France). Analytical grade solvents used such as acetone (ACE) and n-hexane (HEX) were also purchased from VWR International (Fontenay sous bois, France), Fontainebleau sand was provided by Carlo Erba reagents (Milan, Italy). Alumina, Silica-gel 60 (200–300 mesh) and anhydrous sodium sulfate (Na_2SO_4) were purchased from VWR International. Certified reference material (CRM HS-5) of marine sediment was purchased from National Research Council (Canada).

Sample Extraction and Analysis

Sediments (10 g) were thoroughly mixed with anhydrous Na_2SO_4 and 2.5 g of activated copper powder (removal of elemental sulfur). Sediments were then spiked with 1 $ng.g^{-1}$ dry weight (dw) surrogate solution (endrin ketone and PCB 204) and extracted with a 'Soxtherm' device (C. Gerhardt KG, Germany). The program steps were extraction by immersion of the sample in hot solvent (HEX:ACE, 50:50) at 120°C during 65 min and then under reflux of distillated solvent for 90 min. The extracts were then fractionated and eluted according to Dierking et al. (2009). Quantitative analyses of OCs and PCBs were carried out using a gas chromatograph (GC) equipped with a GC auto-sampler, split/splitless injector and coupled with a mass spectrometer (Perkin-Elmer Autosystem XL, California, USA). The separation was achieved with a fused silica capillary column (Elite-5MS, 30 m×0.25 mm ID with 0.25-µm thickness film Perkin-Elmer, California, USA). Helium was used as carrier gas at a constant rate of 1 ml min^{-1}. The temperature program during the run was as follows: initial temperature 50°C, then increased to 100°C at 30°C min^{-1} and increased to 290°C at 3°C min^{-1}, held for 5 min. The injector was set at 250°C, and the MS source at 300°C. MS was operated in positive electron ionization (EI) mode (70 eV) using SciFi mass spectra acquisition corresponding to simultaneous full scan (FS) and selected ion resolution (SIR) mode. OCs and PCBs were determined using mirex as internal standard.

Quality control and quality assurance

All data were subject to quality assurance and control procedures. All concentration data are based on dw. The detection limit of organochlorine compounds ranges from 20 to 26 $pg.g^{-1}$ and more specifically 10–30 $pg.g^{-1}$ for DDT class compounds, 5–20 $pg.g^{-1}$ for HCH class compounds, and 5–26 pg g^{-1} for PCB congeners. Endrin ketone and PCB 204 were used to measure the recoveries for OCs and PCBs, respectively. The spike recoveries for OCs and PCBs in CRM marine sediment (HS-5) ranged from 85% to 99% and from 94% to 101%, respectively.

2.3.3. Alkylphenols

Chemicals

4-tert-Octylphenol, 4-n-Octylphenol and Nonylphenol technical were purchased from Dr. Ehrenstorfer. The standard solutions were prepared in methanol. The analytical grade solvents used such as diethyl ether, methanol, dichloromethane were purchased from VWR International (Fontenay Sous Bois, France). Acenaphtene as internal standard was obtained from Sigma Aldrich, France. The 3 ml of 200 mg of Chromabond HR-X SPE sorbent cartridges were purchased from Macherey-Nagel (France).

Sample preparation

Pressurized liquid extraction

All the glassware was washed and then heated at 300°C for 12 hours prior to use. Ten gram of dried solids samples were placed in a cylindrical glasses cells and extracted using a Soxtherm Solvents Extractor (Model Gerhardt type Multistat 50 – 60, Germany). Each extraction began with 4 min preheating time followed by 5 min heating and then 5 min static extraction with methanol. The static extraction was performed at constant temperature (120°C, 6900 kPa), 2 cycles extraction was used. The extract (~45 ml) was reduced using rotary evaporation to less than 35 mL then top up to 35 mL with methanol and finally placed into 100 ml calibrated flask and top up to 100 ml with water (Jimenez-Diaz, 2010).

Solid-phase extraction

The analysis processing is described in details elsewhere (Jimenez-Diaz *et al* 2010) with minor modification. Briefly, the extract underwent SPE on an Isolute ENV + Cartridge previously activated with diethyl ether (5 ml), methanol (5 ml) and water (5 ml). The extracts (100 ml) were passed through the cartridges at a flow rate 2 – 3 ml.min^{-1}. The first fraction elution for a clean-up procedure and was performed by passing 5 mL of methanol/water 20:80(v/v) and then the cartridge was dried under vacuum for 15 min. Second fraction containing the targeted compounds, was performed with 5 mL of diethyl ether/methanol 90:10 (v/v). Elution were evaporated to dryness at room temperature under a stream of nitrogen.

Furthermore, 250 µl dichloro methane containing 20 µl of acenapthene as internal standard and 40 µL of BSTFA/TMCS 90:10 (v/v) were added to the vial in order to carry out the redisolution and the derivatization of the residue. Next, vials were closed, heated at 50°C during 5 min to complete the derivatization process. After this reaction, 2 µl of the product was injected into GC-MS system.

Gas-Chromatographic analysis

The quantitative analysis of APs were carried out using a Gas Chromatograph (GC) equipped with a GC auto-sampler, split/splitless injector and coupled with a mass spectrometer (Perkin-Elmer Autosystem XL, California, USA). The separation was achieve with a fused silica capillary column (Elite-5MS, 30 m x 0,25 mm ID with 0,25 µm thickness film Perkin-Elmer, California, USA). The oven temperature was programmed to increase from 85 – 130°C within 10°C.min^{-1} and increased to 300°C at 6°C.min^{-1} held for 2,5 min. The injector was set at 300°C and the MS source at 230°C.

2.3.4. Granulometric Analysis

Sediment samples were prepared from AR grade calcium carbonate (minimum 99.5% $CaCO_3$). This was ground for fifteen minutes using a glass pestle and mortar to breakdown any aggregated that may have formed during storage. Approximately 10 gram of samples was removed to a small porcelain crucible and 'Calgon'solution added one drop at a time until a thick plastic paste formed. Dry samples are not particularly suited to particle size analysis – they tend to show distinct grain size sorting, leading to problem in accurate sub-sampling.

Particle size was measured using a Beckman-Coulter LS 230 laser particle size analyzer, equipped with a fluid module. This uses a 5mW, 750 nm laser beam and 126 detectors placed at a range of angles up to 35° to the laser beam. The LS 230 measures particle sizes in two ways, using the Fraunhofer and Mie theories of light scatter.

Conventional (Fraunhofer) laser diffraction is used to measure particle in size range 2 mm to 0.4 µm. The Fraunhofer theory relies on the fact that when light from a laser is shone at a particle, some of it is diffracted. The amount of diffraction is dependent upon the size of the particle. The smaller the particle, the greater the maximum angle of diffraction. Thus, particle of different sizes each produce a characteristic diffraction pattern.

A second unit measures particle size down to 0.04 µm using a proprietary technique that Coulter refer to as PIDS (Polarisation Intensity Differential Scatter). This is also based on laser diffraction, but measures light flux only at high angle to the beam. Using six detector and tungsten light sources, the PIDS unit compares the intensity of light scatter at two polarization angles, at three different wave lengths (450, 600 and 900 nm), allowing measurement in the range 0.04 – 2000 µm. Measuring the size of a single particle in this way is relatively simple, but measuring a mixture of particles of different sizes requires mathematical modeling. The LS 230 applies a user-specified optical model to distinguish between the signals from each particle in the sample. The model is applied post-measurement, so that the choice at analysis time is not critical.

Interpolation of the LS230 output was carried out using version 3.01 of the Coulter LS Control Software. Statistical analysis of the resulting data was carried out using Minitab version 11.

2.3.5. Minor and trace elements analysis

These data were collected by Oursel et al (2014) under permitted by the authors.

Particulate elements (Al, Li and Pb,) were quantified from the acid-digested filters by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS Element 2, Thermo Finnigan). The instrument was calibrated using standard solutions and an In was added as internal standard in each sample (Lenoble *et al* 2013). Quality control of HR ICP-MS measurements was checked by the determination of elements concentration on Certified Reference Material (SLRS-4 river water, LGC6187 river sediment, National Research Council Canada). All results presented good agreement with the certified data. Results obtained for LGC6187 (triplicate) showing that the values obtained for most of the studied elements fall in 90 - 110% of yield.

CHAPTER III

INDICATORS OF TERRESTRIAL BIOGENIC HYDROCARBONS CONTAMINATION AND LINEAR ALKYLBENZENES AS LAND-BASE POLLUTION IN MARINE SEDIMENTS

Agung Damar SYAKTI, Laurence ASIA, Fehmi KANZARI, **Halikuddin UMASANGAJI,** Stephanie LEBARILLIER, Benjamin OURSEL, Cedric GARNIER, Laure MALLERET, Yann TERNOIS, Gilbert MILLE, Pierre DOUMENQ

SUMMARY

The hydrocarbons derive from very varied origins and massively recognized especially in the marine environment. Some of these ubiquitous compounds are carcinogenic, mutagenic and can cause adverse effects to the marine ecosystems. Additionally, marine sediments are widespread to be an excellent trap for pollutants such as hydrocarbons. Numerous works have been conducted on the concentration levels of these chemicals with the different values and modes of distribution. Nevertheless, to the best of our knowledge, there have not been published works on linear alkyl benzenes (LABs) in this particular area. Moreover, even if LABs are present in small amounts in some crude oils, the presence of various alkyl benzenes in sediments is not directly related to contamination by petrogenic or pyrolytic sources but rather is due to their use as precursors in the industrial synthesis of linear alkyl benzene sulfonate (LAS) detergents (Mungray and Kumar 2009 ; Ishiwatari *et al* 1983).

In this third chapter, we will first describe the levels of n-alkanes, PAHs, and their spatial distributions through the plume of WWTPs. We will also attempt to determine their relationships with Total Organic Carbon (TOC) which plays a necessary role in terms of adsorption process organic materials. The distributions of n-alkanes at the 12 stations near the WWTP range from 34.2 to 2155.8 µg.kg^{-1} with the mean value of 941.25 µg.kg^{-1}. According to the statistical analysis, we found that there is a weak positive correlation between n-alkanes and TOC on the majority stations except the P7, P8 and P9 stations, particularly the stations that are closer to the WWTP. This shows that probably the n-alkanes in these latter stations derive from other sources compared to others. In addition, the majority of stations in the east have the highest concentrations compared to other stations in the west, which is a proof that 85% of plume deflection towards the east side.

Subsequently, we also characterized the sources and origins of these hydrocarbons by employing several indices that have been used by previous investigators to determine their origins either petrogenic or pyrolytic. These are alkane/C_{16}, NAR, CPI, UCM/R, LMW/HMW (Biogenic and Petrogenic Discrimination). Moreover we analyzed Pr/Phy, n-C_{17}/Phy, TAR, n-C_{29}/n-C_{17} and since no ratio is absolute we have analyzed several indices to have the most accurate results that give us the mixed origins. Although several clues provides the petrogenic origins, most of the evaluations show the origin biogenic that are characterized by the terrestrial input. In the other side, several of biogeneic origins also originate from sedimentary bacteria, marine animals and higher plants. Also, the bi-dimensional analyzed classified these n-alkanes as the biomass combustion origin. Despite, the ratio between UCM/R and NAR demonstrated the majorities of the stations are characterized by the combustions of the oils.

Regarding the distribution of PAHs in the 12 stations of our study site we measured the concentrations from 696.4 to 10699.4 µg.kg^{-1} with the average value of 3620.8 µg.kg^{-1}. We have statistically found a positive correlation in terms of the distribution of these PAHs with TOC except

for the P4 and P8 stations, which implies that TOC plays an important role in the sorption of organic materials in the sediment surface. The highest concentrations are found in the P4 stations which is closer to the WWTP and Station P7 which is offshore. This suggested that there is no special trap at the level of distribution of PAHs. Nevertheless, we have found that there was a trend enrichment of PAH concentrations in the stations situated in the east which were also found for n-alkanes. As our previous explanation that this phenomenon is due to the majority deviation of plume towards the direction of the east. These PAHs individuals are predominated by the Fl, B (a) Pyr isomers, B (a) Ant and Chr. In addition, the areas from which the richest of PAHs are signalized by the Fl isomer.

In order to determine the sources and origins of PAHs, we used some clues such as Phen/Ant, Fl/Pyr, bi-dimensional Ant/Σ178, Fl/Σ202 and the triangle diagram that was proposed by Budzinski *et al* 1997. This diagnosis has shown that PAHs on the sediment surface of Cortiou are derived from mixed sources either petrogenic or pyrolytic. On the other hand, they are characterized by the biomass combustions.

In order to be able to have the contamination levels of these hydrocarbons, we evaluated the sediment qualities in our study site using ERL (Effects Ranges Low) and ERM (Effects Ranges Medium) proposed by Long and USEPA 1995). We found that the majority of stations are classified below ERL (4.02 mg.kg^{-1}). While the P4, P6 and P7 stations exceed this ERL. This shows that the most of these stations are probably not contaminated by these PAHs except the last three stations especially for the benthic ecosystem.

In this work, we have also been able to demonstrate the levels of linear alkylbenzenes (LAB) concentrations on the sediment surface at Cortiou and the determination of the efficiency of the wastewater treatment plant through the quantification of the ratio of I/E of these compounds. Total concentrations of homologous LABs in sediment surfaces ranged from 43 to 502.3 µg.kg^{-1} with an average value of 175.10 µg.kg^{-1}. These substances are predominant by 5-C_{12}, 4-C_{12}, 5-C_{11} which shows that they are the most used in the detergent industries. In the other side, LABs show statistically that most stations have positive correlations with TOC. This explains that TOC play an essential role in terms of these organic contaminants sorption in marine surface sediments. Then, the I/E reports demonstrated that the process of biodegradation of these molecules is incomplete. Nevertheless, this finding provides an approximate trap that the deposits integrate a signal more than 7 years. This shows that the possibility of LABs deposited before the installation of the geolide and impossible to conclude on the effectiveness of the work of the WWTPs currently.

This article was published in "International Journal of Environmental Science and Technology" 2012. This is a summary of the main work carried out in this study.

It became important from this information to deepen the study by accompanying with some physical information that led us to describe the profiles of the distributions of these compounds related to these parameters and the dominant deflection of the plume which strongly influenced by the wind direction, turbulence and local upwelling.

.

INDICATORS OF TERRESTRIAL BIOGENIC HYDROCARBONS CONTAMINATION AND LINEAR ALKYLBENZENES AS LAND-BASE POLLUTION IN MARINE SEDIMENTS

A. D. Syakti L. Asia F. Kanzari **H. Umasangaji**
S. Lebarillier B. Oursel C. Garnier L. Malleret Y. Ternois G. Mille P. Doumenq

Abstract

Aliphatics (n-alkanes) and polycyclic aromatic hydrocarbons (PAHs) were measured in surface sediments collected from 12 sampling points (P1–P12) of sewage discharge to the sea from the wastewater treatment plant of Cortiou (France). Total n-alkanes and PAHs concentrations ranged from 34 to 2,155 and 696 to 10,700 µg kg^{-1}, respectively. Some specific hydrocarbon indexes suggested that terrestrial biogenic inputs are predominant compared to marine sources and that pyrolytic sources derived from wood and biomass combustion contribute to PAHs in the surface sediments. Total linear alkyl benzenes in Cortiou sediments ranged from 42.9 to 502.3 µg kg^{-1}. Low internal and external (I/E) isomers ratio (P0) suggests that in adequately treated sewage is discharged into the marine environment while some environmental processes might change I/E ratios during transport seaward (P1–P12). The high contaminant levels followed by the cumulative concentration of several compounds may lead to elevated toxicity levels in the sediments.

Keywords : Organic contaminants, n-Alkanes, Polycyclic aromatic hydrocarbons, Linear alkyl benzenes, Environmental monitoring, Wastewater treatment discharge.

3.1. Introduction

The Bay of Marseille is one of the most urbanized sites in the Mediterranean region. A large number of industrial and domestic wastes are discharged into the bay, which contains considerable quantities of pollutants that enter the marine environment via various routes. Primary potential pollution sources are the urban wastewater treatment plant (WWTP) ‘‘Géolide,’’ with an average discharge of 4 m^3. s^{-1}, the Marseille channel and runoff from the Huveaune River, which passes through many industrial sites. During periods of intense rain, excess rainfall is channeled through Cortiou. The site studied in this research is located in the center of the ‘‘Calanque National Park’’ and encompasses the Friou archipelago, Plane, the Marseilleveyre islands and Cap Croisette up to Green Island. The National Park, which was established in June 2012, is the first suburban national park in Europe. Land- and seabased sources of petroleum hydrocarbon pollution in this area have been identified in previous studies (Mille *et al* 2007; Asia *et al* 2009). However, to the best of our knowledge, there are no published data for linear alkyl benzenes (LABs) in this specific area. Moreover, even if LABs are present in small amounts in some crude oils, the presence of various alkyl benzenes in sediments is not directly related to contamination by petrogenic or pyrolytic sources but rather is due to their use as precursors in the industrial synthesis of linear alkyl benzene sulfonate (LAS) detergents (Ishiwatari *et al* 1983; Mungray and Kumar 2009). Here, our goals are to characterize the occurrence and extent of (1) petroleum hydrocarbon pollution in Cortiou sediments, particularly n-alkane and polyaromatic hydrocarbons (PAHs) pollution, and (2) ‘‘sewage tracer’’ compounds, such as LABs, as by-products of LAS detergents, which are the most widely used anionic surfactants (Leon *et al* 2000). Another goal of this study is to determine whether municipal water discharge is responsible for the presence of these pollutants by determining the concentrations and distributions of individual n-alkanes, 16 EPA priority PAHs and LABs in surface sediments of the Cortiouin relation to the carbon content and organic carbon in the sediment (Hinga 2003; Rico-Rico *et al* 2009). This study was performed in 2010–2011 in the Environmental Chemistry Laboratory, Aix-Marseille University, France.

3.2. Materials and methods

Chemicals SupraSolv grade (Merck, Darmstadt, Germany) solvents such as acetone (AC), dichloromethane (DCM) and nhexane (HEX) were purchased from VWR International (Fontenay Sous Bois, France). Acetonitrile of high-performance liquid chromatograph (HPLC) grade (Merck) and water purified with a Milli-Q system (Millipore, Bedford, MA, USA) were used throughout the liquid chromatography analysis. The reference standard mixture containing 16 US EPA priority PAHs, namely naphthalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo(a)anthracene (B[a]Ant), chrysene (Chr), benzo(b)fluoranthene (B[b]Fl), benzo(k)fluoranthene (B[k]Fl), benzo(a)pyrene (B[a]Pyr), indeno (1,2,3-cd) pyrene (Ind), dibenzo(a,h)anthracene (dB[ah]Ant) and benzo(ghi) perylene (B[ghi]P), at concentration levels between 100 and 2,000 mg mL^{-1} in methanol/dichloromethane (1:1;v/v) was obtained from Supelco (Bellefonte, PA, USA). Labeled n-alkane (n-nonadecane-d40) and 1-phenylnonane were purchased from Sigma-Aldrich, St. Louis, MO, USA. Standard working solutions were diluted by DCM. A standard certified reference material (harbor marine sediment HS-5) was obtained from Laboratory of the Government Chemist (LGC) Promochem.

Fontaine bleau sand was provided by Carlo Erba reagents (Milan, Italy). Alumina, silica-gel 60 (200–300 mesh) and anhydrous sodium sulfate (Na_2SO_4) were purchased from VWR International. The alumina and silica-gel silica was deactivated with 5 % water (w:w), and Na_2SO_4 was baked for 48 h at 550ºC before use. Analytical reagent grade of glucose and H_3PO_4 were purchased from Fisher Scientific. $NaHCO_3/Na_2CO_3$ was supplied from Shimadzu.

Sample collection

As shown in Figure 3.1, sediments from 12 sampling points (three independent subsamples per point; P1–P12) were collected in front of the WWTP sewer outfall of Cortiou-Marseille, France. One additional point has been collected in the wastewater treatment sewage canal (P0). Surface sediment samples were collected with a sediment grab sampler (Shiptex; Wildco Inc, USA) and PVC core samplers (100 mm diameter) using Scuba equipment on March 21 and June 23, 2010. The sampling points were collected in a line perpendicular to the coastline (direction 237°N) starting from the sewer outfall (with low salinity) and moving out toward the sea, up to the limit of WWTP sewage discharge influence. All sediment samples were freeze-dried, sieved using a 2-mm mesh, homogenized and stored at -18ºC prior to analysis.

Sample extraction and analysis

The sample extraction and analysis were conducted according to Kanzari *et al* (2012) and Syakti *et al* (2013). Briefly, 10 g of freeze-dried sediments was transferred to a precleaned cellulose extraction thimble and extracted using a Soxhlet extractor apparatus for 16 h with a 200 ml mixture of DCM and HEX (1:1, v/v). Prior to extraction, nonadecane-d_{40} was added to the samples as an internal standard (IS) for n-alkane quantification.

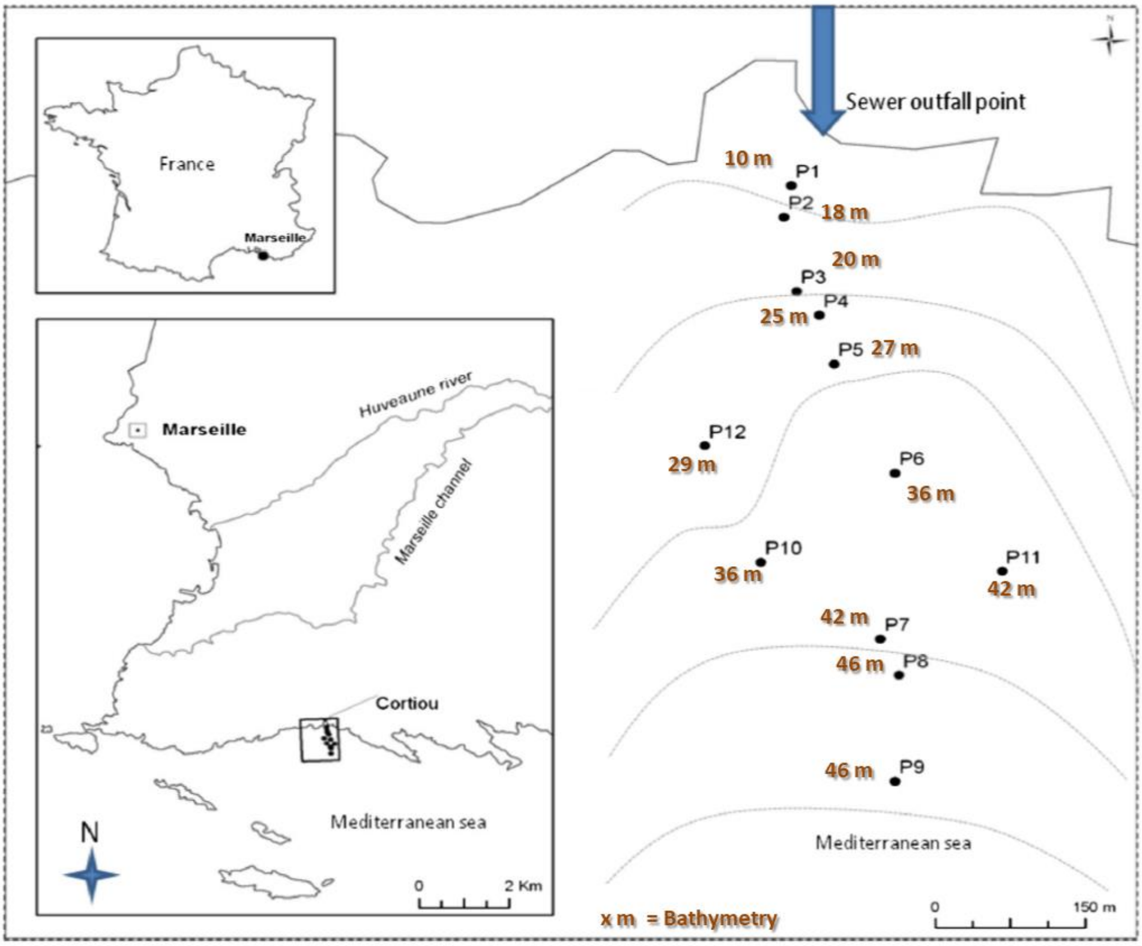


Figure 3.1. Site location and sampling stations.

All or part of the extractable organic matter (EOM), depending on the initial weight, was dissolved in n-hexane and applied to a 50 % alumina 50 % silica (8 g of each, both deactivated with 5 % H_2O) chromatography column (30 9 1 cm). The saturated fraction (F1) was first eluted with 30 ml of HEX. Elution with 20 mL of HEX/DCM (9:1) and 40 mL of HEX/DCM (4:1) was combined to yield the aromatic fraction (F2). Sulfur interference was removed by shaking the extract with copper powder previously reduced with diluted hydrochloric acid (0.1 M) (Blumer, 1957). A labeled n-alkane (n-nonadecane-d_{40}) was added to each sample and the matrix blank prior to extraction as surrogate to assess the overall procedural recovery. In this study, n-alkane surrogate recoveries were 98 to 102 %. Concerning PAHs, an HS-5 certified sediment was analyzed to evaluate the extraction accuracy. Reproducibility estimated for PAHs on triplicate samples was > 90 %. Each fraction was evaporated on a rotary evaporator and under a gentle stream of nitrogen, and the dry residue was weighed (microbalance, Perkin–Elmer AD2Z). The sum of the aliphatic and the aromatic fractions gave the total hydrocarbon content (THC). F1 was diluted in HEX, and the n-alkanes present were separated by capillary gas chromatography (GC) under the following equipment: GC Autosystem XL Perkin Elmer chromatograph with on-column injection and a Perkin Elmer Elite-XLB column (30 m x 0.25 mm ID x 0.25 µm film thickness). Helium was used as the carrier gas at a constant rate of 1 ml min^{-1}.

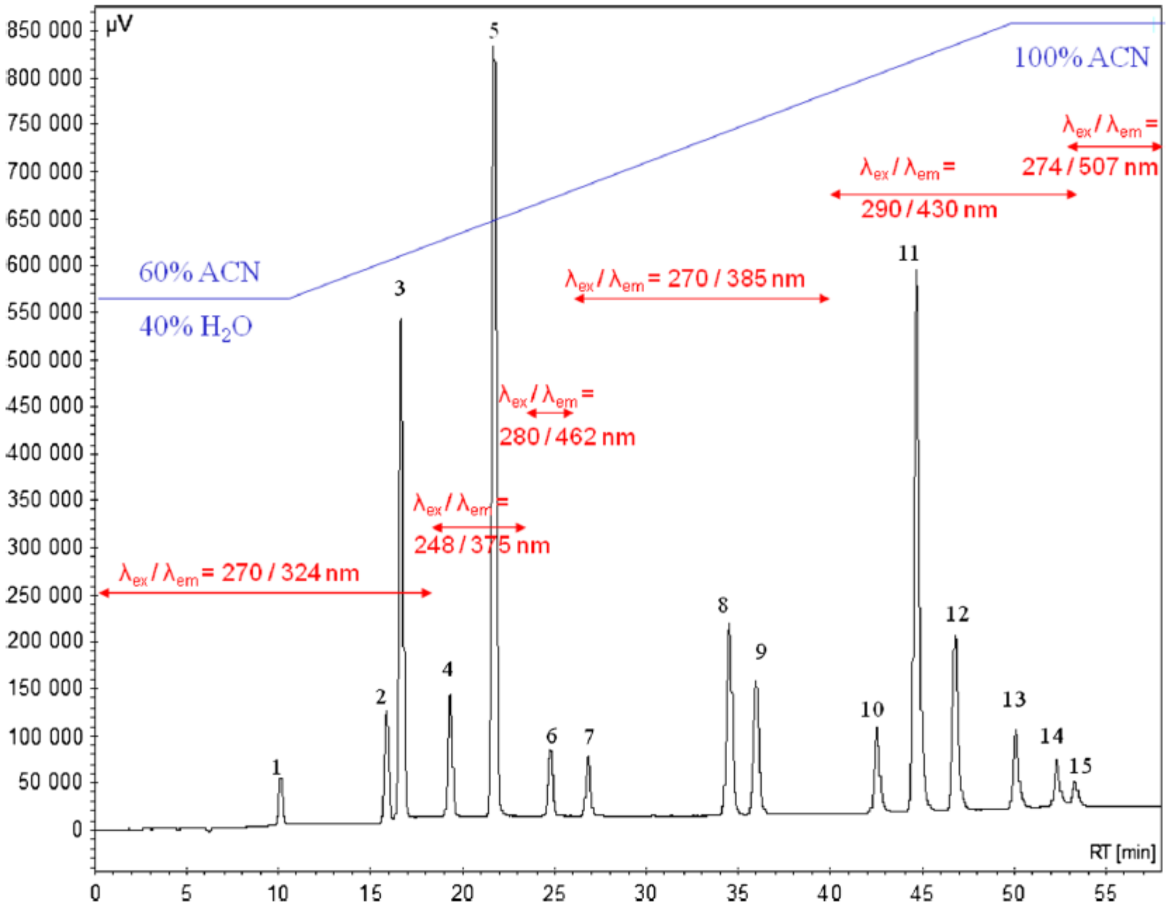


Figure 3.2. HPLC–PFD chromatogram obtained from Cortiou sediments. Peak identities are (1) naphthalene (Na), (2) acenaphthene (Ace), (3) fluorene (F), (4) phenanthrene (Phe), (5) anthracene (Ant), (6) fluoranthene (Fl), (7) pyrene (Pyr), (8) Benzo(a)anthracene (B[a]Ant), (9) chrysene (Chr), (10) benzo(b)fluoranthene (B[b]Fl), (11) benzo(k)fluoranthene (B[k]Fl), (12)benzo(a)pyrene(B[a]Pyr), (13)indeno (1,2,3-cd) pyrene (Ind), (14) dibenzo(a,h)anthracene (dB[ah] Ant) and (15) benzo(ghi) perylene (B[ghi]P). The excitation (kex) and emission (keM) wavelength program to determine individual PAHs and gradient elution program using solvent with fluorescence detection following liquid–liquid A (Acetonitrile) and solvent B(Water).

The temperature was programmed from 70 to 285°C (5°C min^{-1}) and then held for 30 min. The mass spectrometer was operated in the electron impact ionization (EI) mode (70 eV) and simultaneously scanned in both Full Scan and Selected Ion Monitoring (SIM) modes. LAB identification relied on both retention times and characteristic ions. The 91 m/z ion was used for quantification, and the 105 and 119 m/z ions were used for confirmation with 1-phenylnonane as internal standard. Conventionally, these isomers are described using the form n-Cm-LAB, where n = the position of the benzene ring and m = the number of carbon atoms in the aliphatic chain. Aromatic hydrocarbons (PAHs) contained in F2 were analyzed using a Prostar (Varian, Palo Alto, CA, USA) HPLC equipped with a thermally controlled autosampler and a programmable fluorescence detector (HPLC–PFD). Excitation/emission time windows for the fluorescence detector are described in Figure 3.2 The injection vial and the analytical column were maintained at 10 and 35°C, respectively, for all analyses. The separations were carried out using a reverse-phase C_{18} column (250 mm x 4.6 mm x 5 µm, ChromSpher 5PAH, Varian) protected by a C_{18} guard column (10 mm 9 3 mm, 5 lm, Chromguard). Aliquots of 20 lL were injected, and the flow rate was held at 1.2 mL min^{-1} for a total run time of 55 min. The data were acquired and processed using the Galaxie ™ software package (Varian). The total carbon (TC) content was determined using the high-temperature (900ºC) catalytic oxidation method with IR detection of CO_2 (Benner and Strom 1993). The inorganic carbon content was determined after addition of H_3PO_4 at 200ºC followed by IR quantification of CO_2, calibrated using $NaHCO_3/Na_2CO_3$. The total organic carbon (TOC) content was calculated by content. All data in this work concerning in sediment (µg.kg^{-1}) were expressed related to dry weight sediment.

Statistical analysis

The analysis of variance (ANOVA) and linear regression were employed to compare differences in Σ n-alkane, ΣPAHs and ΣLABs with the physicochemical properties (EOM, TC and TOC) in the surface sediments of Cortiou and to explore correlations between these parameters. A p value of 0.05 or less was regarded as being significant for all the tests. The statistical analyses were implemented using the SigmaPlot for Windows® version 11.0 (Systat Software, Inc., wpcubed, GmbH, Germany).

3.3. Results and discussion

3.3.1. n-Alkane

n-Alkane occurrence in Cortiou sediments Table 3.1 summarizes petroleum hydrocarbon contamination in Cortiou surface sediments. As shown, EOM can be used as an indicator of organic material input in the environment. The EOM concentrations ranged from 352 to 7,525 mg kg^{-1} with an arithmetic mean of 1,739 mg kg^{-1}. These values are significantly higher than those previously reported close to the Cortiou area, which ranged from 40 to 300 mg.kg^{-1} (Mille *et al* 2007; Asia *et al* 2009). This elevated range of EOM may indicate surface sediment that is highly polluted with organic materials but is not necessarily contaminated with hydrocarbons. Indeed, THC/EOM ranged from 60.5 to 84.6 % (Table 3.1), compared to 52 % for sediments chronically contaminated with petroleum hydrocarbons (Mille *et al* 2007). For the latter sediments, F1 fractions represent approximately 80 % of the total hydrocarbons and are markedly higher (1.9–4.9 times) than F2 fractions. Total n-alkanes (Table 3.2) ranged from 342 to 2,155 µg kg^{-1}, except for P9 (34 µg kg^{-1}). Several authors have used indexes to assess the origins of hydrocarbons based on geochemical markers such as Pn-alkane/nC16, low/high molecular weight (LMW/HMW), the Carbon Preference Index (CPI), the natural n-alkanes ratio (NAR), the terrigenous/aquatic ratio (TAR) and the simple ratio of nC_{29}/nC_{17} (Bourbonniere and Meyers 1996; Mille *et al* 2007; Asia *et al* 2009). According to these authors, petroleum-contaminated samples displayed P n-alkane/nC16 values\15, while biological samples had values higher than 50. The application of this ratio to Cortiou sediments (Table 2) showed a predominant biogenic input, as evidenced by the high values (200). Furthermore, the LMW/HMW ratio confirmed this trend with values largely below 0.2. Such ratio values have been reported for biogenic sources issued from sedimentary bacteria, marine animals and higher plants (Jeng 2006; Syakti *et al* 2013). The CPI indicates the ratio between odd- and even-numbered n-alkanes (Budzinski *et al* 1997). In the range C_{11}–C_{35}, CPI values close to one are characteristic of crude oils and petroleum hydrocarbons (Volkman *et al* 2008). For most stations, CPI values ranged from 1.8 to 4.6 (average 2.6), with a predominance of nC_{25}, nC_{27}, nC_{29}, nC_{31} and nC_{33} n-alkanes confirming a biogenic input, presumably released during plant wax degradation (Volkman *et al* 2008). CPI values <1 were measured at station P9, showing a weathered profile of aliphatic hydrocarbons (Asia *et al* 2009; Micic *et al* 2010).

Tabel 3.1. Gravimetric analysis, total carbon (TC) and total organic carbon (TOC) content data for Cortiou sediments.

Cortiou points	EOM (mg.kg^{-1})	F1 (mg.kg^{-1})	F2 (mg.kg^{-1})	THC (mg.kg^{-1})	THC/EOM(%)	F1/THC(%)	F2/THC(%)	F1/F2	TC(%)	TOC (%)
P0	352.2	196.7	99	262.7	74.6	74.9	25.1	3	11.2	0.8
P1	554	316.8	79.2	396	71.4	80	20	4	8.1	1.9
P2	355	186.9	28	215	60.5	87	13	6.7	9	0.5
P3	853	431	155.2	586.2	68.7	73.5	26.5	2.8	8.4	1.1
P4	1,553	844.7	252.3	1,097.10	70.6	77	23	3.3	7.9	2.6
P5	1,476	847.6	219	1,066.70	72.3	79.5	20.5	3.9	7.2	1.7
P6	730	475.4	139.3	614.8	84.3	77.3	22.7	3.4	8.2	3.1
P7	7,525	5,209.30	1,157.60	6,366.90	84.6	81.8	18.2	4.5	11.6	7.4
P8	3,706	2,354.60	540.4	2,895.00	78.1	81.3	18.7	4.4	12.9	8.8
P9	2,819	1,952.40	400	2,352.40	83.4	83	17	4.9	10.5	4.9
P10	390	178	93.2	271.2	69.6	65.6	34.4	1.9	7.9	1.3
P11	416	238.9	79.6	318.6	76.6	75	25	3	8.1	0.8
P12	496	278.3	95.7	373.9	75.4	74.4	25.6	2.9	8.4	1.6

TC and TOC are expressed from mg.C.mg^{-1} of dry sediment with an accuracy of ±0.1 mg.C EOM extractable organic matter, F1 saturated hydrocarbon fraction, F2 polycyclic aromatic hydrocarbon fraction, THC total hydrocarbon content, TC total carbon, TOC total organic carbon.

As previously proposed by Mille *et al* (2007), the NAR was used to roughly estimate the proportions of natural and petroleum n-alkanes. Values from 0.3 to 0.6 were observed, indicating biogenic sources such as higher terrestrial plants or marine plants, rather than the zero values displayed by petroleum hydrocarbons and crude oils (Kanzari *et al* 2012; Wagener *et al* 2012). Another index used to discriminate terrestrial from marine inputs is the TAR (Bourbonniere and Meyers 1996), the ratio of long chain odd-numbered n-alkanes (nC_{27} + nC_{29} + nC_{31}) to short-chain odd-numbered n-alkanes (nC_{15} + nC_{17} + nC_{19}). For this index, values ranging from 4.8 to 40.4 were observed, characteristic of important terrigenous inputs (Figure 3.3a). Moreover, since n-C_{29} is abundant in land plants and n-C_{17} is prominent in marine organisms, the ratio of these two alkanes reflects the relative contributions of allochthonous and autochthonous hydrocarbons to the sediment. Thus, they were used to discriminate between terrestrial and marine inputs (Bourbonniere and Meyers 1996; Sikes *et al* 2009). A value of approximately 1 for this ratio indicates marine sources. Cortiou sediments yielded values between 4 and 87, clearly indicting the predominance of terrestrial sources (Figure 3.3a).

3.3.2. PAHs

According to Baumard *et al* (1998), sedimentary PAHs levels can be characterized as low, moderate, high and very high when total PAH levels (of the 16 EPA priority PAHs) are in the ranges of 0–100, 100 – 1,000, 1,000 – 5,000 and > 5,000 µg.kg^{-1}, respectively. A PAH level below 100 µg.kg^{-1} is indicative of sediment with low pollution, whereas values higher than 1,000 µg kg^{-1} correspond to chronically polluted industrialized areas or harbors. In this work, total PAH concentrations varied from 696 to 10,699 µg kg^{-1} with an arithmetical mean of 3,621 µg.kg^{-1}, corresponding to sediments with pollution in the upper-middle range. Aromatic fractions of sedimentary hydrocarbons were dominated by PAHs with four to five condensed aromatic rings, such as fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, chrysene and benzo[a]anthracene, with average concentrations of 589, 486, 480, 443 and 361 µg.kg^{-1}, respectively (Table 3.3). Other PAHs containing four to six condensed rings, such as pyrene, benzo[g,h,i]perylene, benzo[a]fluoranthene, indeno(1,2,3-cd)pyrene and dibenzo[a,h]anthracene, were found with average concentrations of 336, 250, 232, 201 and 44 µg kg^{-1}, respectively. Except for phenanthrene, whose average concentration was 176 µg.kg^{-1} (Table 3.3), aromatic fractions were characterized by low concentrations of two to three condensed rings, such as naphthalene, acenaphthene, fluorene and anthracene, which were found at concentrations <15 µg.kg^{-1} dw.

Tabel 3.2. Index used to elucidate hydrocarbon input in marine sediment of Cortiou WWTP sewer

Cortiou's station	**P0**	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**	**P11**	**P12**
Total n-alkanes (µg.kg^{-1})	187.5	918	1,248.80	964.3	1,608.70	1,320.90	2,155.80	127.90	417.50	34.20	342.20	757.60	1,399.20
Total n-alkanes/n-C_{16}	1,019	582	725	931	274	682	2,075	210	247	282	831	1,770	1,019
LMW/HMW	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.01
NAR	0.4	0.6	0.6	0.3	0.6	0.5	0.5	0.5	0.5	0.4	0.3	0.3	0.4
CPI	1.9	3.5	4.6	2.5	3.7	3.3	3.3	3	3.4	0.4	1.8	2	2.3
TAR	9.3	22.1	32.3	13.8	17.1	26.5	40.4	25.7	39.1	4.8	8.2	15.1	20.3
n-C_{29}/n-C_{17}	113.3	29.4	41.2	5.9	16.7	33	87.3	30	43.4	4	26.2	38.2	36.2

Total n-alkanes/n-C16 = Σ n-alkanes (C_{11}–C_{35})/n-C16; LMW/HMW = Σ n-alkanes (C11–21)/ Σ n-alkanes (C_{22}–C_{35}); NAR = [Σ n-alkanes (C_{19}–C_{32}) - 2 Σ even n-alkanes (C_{20}–C_{32})]/ Σ n-alkanes (C_{19}–C_{32}); CPI = Σ odd n-alkanes (C_{11}–C_{35})/ Σ even n-alkanes (C_{11}–C_{35}); TAR = Σ odd n-alkanes (C_{27}–C_{31})/ Σ odd n-alkanes (C_{15}–C_{19}) LMW low molecular weight, HMW high molecular weight, NAR natural n-alkane ratio, CPI Carbon Preference Index, TAR terrestrial aquatic ratio.

Such features may reflect pyrolytic sources derived from biogenic and/or petrogenic input. Because the area studied is located near Marseille, with its urban/suburban agglomeration and industries, industrial and vehicle emissions are possible sources of PAHs. A first attempt to determine possible sources of PAHs can be made using the occurrences of dominant PAHs, i.e., fluoranthene, benzo[a]anthracene and chrysene. In this study, fluoranthene varied from 93 to 1,743 µg.kg^{-1}. The high concentrations of fluoranthene were attributed to pyrolytic origin, as reported in some studies mentioning the use of fluoranthene as an indicator of combustion related to vehicle engine sources (diesel or gasoline) (Yunker *et al* 2002; Deng *et al* 2013; Inengite *et al* 2013; Liu *et al* 2013). Furthermore, benzo[a]anthracene, which ranged from 58 to 1,289 µg kg^{-1} has also been used by many authors to characterize areas impacted by traffic emissions (Fromme *et al* 2004). Chrysene levels ranged from 90 to 1,580.2 µg kg^{-1}. Previous studies considered chrysene as an indicator of ‘‘burning’’emissions, such as residential heating, waste incinerators and traffic (Fromme *et al* 2004; Asia *et al* 2009; Liu *et al* 2013). In addition, some studies demonstrated the absence of chrysene in petroleum sources. (Page *et al* 1999) found low concentrations of chrysene in diesel and crude oil compared with other PAHs. The area studied is located in the South of France, near many sites that have been particularly affected by repeated fires (Vergnoux *et al* 2011). Leachates due to rain and river runoff may help pyrolytic PAHs from forest fires reach the Cortiou zone. Through numerous examples in the literature, possible sources of PAHs can be evaluated by calculation of abundance ratios of diagnostic PAHs (Mille *et al* 2007; Wang *et al* 2011). As frequently reported, a Phe/Ant ratio of <10 indicates a pyrolytic origin, while a ratio above 10 indicates a petrogenic origin (Olivella *et al* 2006; Deng *et al* 2013). The results of this study discriminated between petrogenic (P1–P6, P8, P10 and P12) and pyrolytic (P7, P9 and P11) inputs, as shown in Table 3.3. A possible explanation for this concern was recent river runoff and land leaching contamination by petroleum hydrocarbons released by the Cortiou treatment plant. However, some authors stated that the Phe/Ant ratio is not a good indicator for tracing the sources of PAHs because the selective degradation of anthracene (Schutzendubel *et al* 1999) during transport may change the value of the ratio (Tao *et al* 2006; 2007).

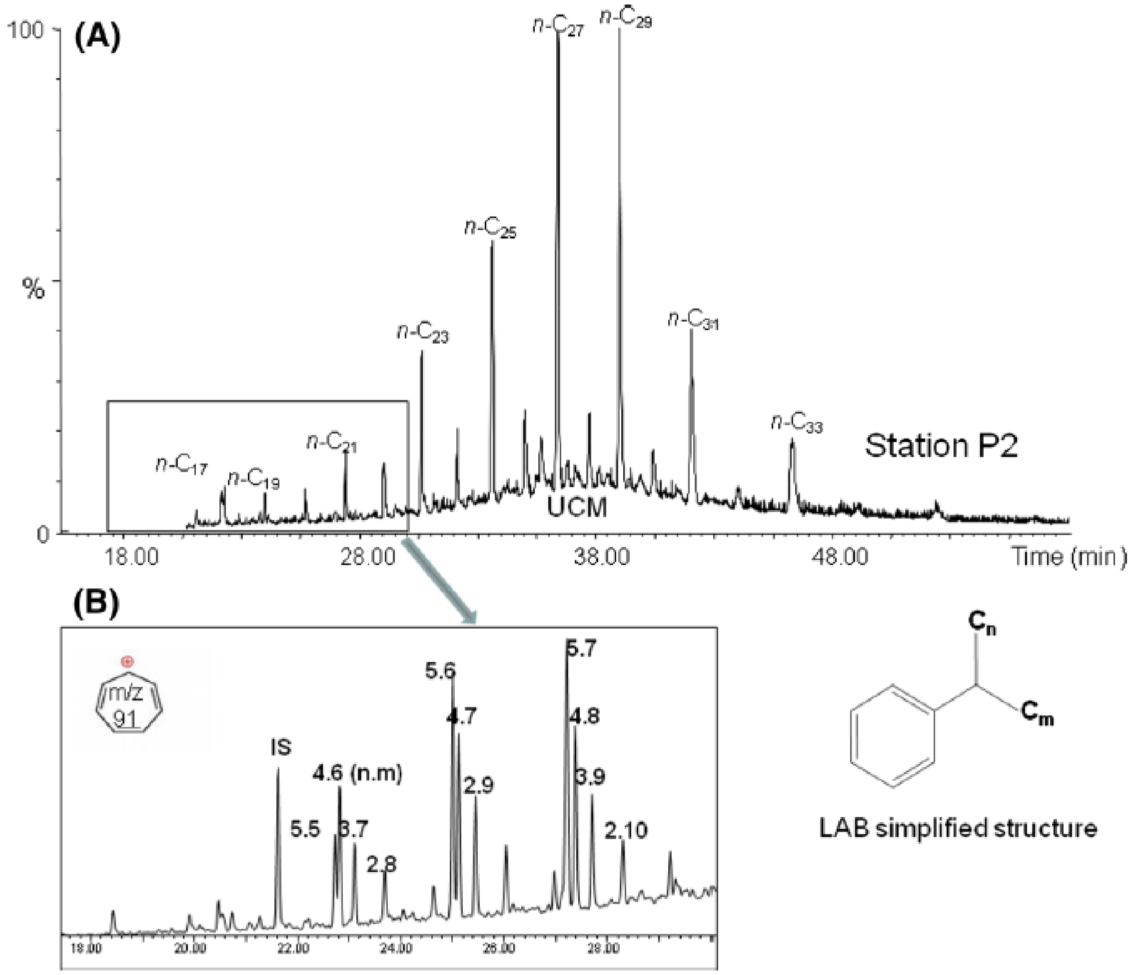


Figure 3.3. GC–MS total ionic current of the saturated hydrocarbon fractions (station P2) with biogenic terrestrial input. UCM unresolved complex mixture (a). SIM fragmentogram using tropylium ion (m/z = 91) of saturated hydrocarbon fractions; n and m indicate alkyl chain lengths on both sides of LAB phenyl groups. IS internal standard (1-phenylnonane) (b).

Consequently, trends shown by Phe/Ant ratios need to be confirmed using other diagnostic ratios. In view of the literature, Fl/Pyr can also be used to distinguish between pyrolytic and petroleum origins (Budzinski *et al* 1997). A value <1 indicates a petroleum origin, while a value >1 suggests pyrolytic contamination (Wang *et al* 2011). In this study, the Fl/Pyr ratio varied from 1 to 7 with an arithmetic mean of 1.9, undoubtedly indicating pyrolytic sources (Table 3.3), except in the case of P9 (Fl/Pyr = 0.9). Figure 3.4 presents a 2D ternary diagram plot of Fl/P202, B[a]Ant/Σ228 and IP/Σ276. As proposed by Budzinski *et al* (1997), a ratio of Fl/Σ202 <0.4 is generally characteristic of petrogenic sources (oil, diesel and coal), a ratio between 0.4 and 0.5 is consistent with liquid fossil fuel (crude oil and vehicle) combustion, and a ratio over 0.5 is generally found in kerosene, grass, coal and wood combustion and creosote.

Table 3.3. PAHs sedimentary content (µg.kg^{-1}) determined by HPLC–PFD

Cortiou's station	P0	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	Average
Na	0.20	nd	1.50	0.20	0.70	0.60	0.80	0.60	0.40	0.20	nd	nd	nd	0.60
Ace	0.60	nd	nd	nd	1.20	nd	0.70	1.50	-	1.30	nd	nd	nd	1.20
F	5.00	0.70	0.10	0.90	63.60	4.50	1.30	2.80	0.60	9.10	0.10	0.10	0.90	7.10
Phe	102.60	40.20	97.00	69.90	1,218.20	256.60	43.50	45.90	15.40	150.00	21.50	24.50	132.10	176.20
Ant	20.00	0.20	-	1.80	72.50	10.20	4.40	14.60	1.50	39.00	1.80	2.60	11.90	13.40
Fl	276.40	93.10	225.90	270.80	2,021.70	723.60	1,742.80	865.20	254.00	370.90	115.70	132.70	253.00	589.10
Pyr	274.30	81.10	168.90	234.70	1,642.40	643.70	251.00	132.70	67.60	390.70	91.20	119.80	203.80	335.60
B[a]Ant	173.90	58.10	22.20	121.20	739.80	313.10	1,089.90	1,289.70	190.70	258.10	59.40	78.70	115.30	361.40
Chr	208.30	90.20	103.60	160.10	945.30	403.90	1,234.40	1,580.20	214.90	291.30	72.40	89.90	130.60	443.10
B[b]Fl	301.70	59.30	102.50	171.50	730.70	419.40	1,207.90	2,043.60	300.50	488.10	83.90	99.70	129.10	486.30
B[k]Fl	158.50	57.10	0.70	92.00	422.70	220.90	580.20	856.90	146.10	242.40	44.60	52.50	70.70	232.20
B[a]Pyr	335.90	109.90	7.80	188.70	777.50	437.30	1,153.20	1,906.20	310.60	522.50	97.10	114.40	141.80	480.60
Ind	98.70	63.20	25.70	105.20	542.50	231.60	245.90	662.20	34.90	51.90	12.80	2.20	15.00	44.40
dB[ah]Ant	32.60	10.20	5.10	16.30	20.00	31.90	104.10	227.90	361.60	289.10	48.10	37.50	30.10	249.80
B[ghi]P	180.30	36.90	53.20	106.10	249.10	182.30	534.90	1,069.40	195.70	113.20	47.90	83.00	93.60	200.80
ΣPAHs	2,168.90	700.30	814.20	1,539.50	9,447.90	3,879.50	8,195.10	10,699.40	2,094.40	3,217.90	696.40	837.60	1,328.00	3,620.80
ΣCPAHs	942.80	300.70	163.30	602.90	2,810.50	1,433.30	3,801.00	6,129.60	1,198.30	1,609.70	301.30	332.50	431.30	1,622.50
Phen/Ant	5.10	201.00	~	38.80	16.80	25.20	9.90	3.10	10.30	3.80	11.90	9.40	11.10	13.10
Fl/Pyr	1.00	1.10	1.30	1.20	1.20	1.20	1.10	6.90	6.50	3.80	0.90	1.30	1.10	1.20

nd (not detected), naphthalene (Na), acenaphthene (Ace), fluorene (F), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo(a)anthracene (B[a]Ant), chrysene (Chr), benzo(b)fluoranthene (B[b]Fl), benzo(k)fluoranthene (B[k]Fl), benzo(a)pyrene (B[a]Pyr), indeno (1,2,3-cd) pyrene (Ind), dibenzo(a,h)anthracene (dB[ah]Ant) and benzo(ghi) perylene (B[ghi]P). PCPAHs = benzo[a]anthracenes + benzofluoranthenes +benzo[a]pyrenes + indeno[1,2,3-cd]pyrenes + dibenzo[a,h]anthracenes

Moreover, a ratio of B[a]Ant/Σ228 < 0.2 implies petroleum sources, a value between 0.35 and 0.7 reflects biogenic combustion, and a value close to 0.9 indicates coal or smelters. Finally, an IP/Σ276 ratio lower than 0.2 is characteristic of petroleum, while a ratio of between 0.2 and 0.5 is consistent with petroleum combustion; moreover, a ratio higher than 0.5 is characteristic of grass/wood/coal combustion (Hartmann *et al* 2004). As a benchmark, P0 was considered mixed petrogenic and pyrolytic origins (Figure 3.4). Considering all of the respective diagnostic ratios together (Figure 3.4), most sediment samples from Cortiou were projected to be in the pyrolytic zone with significant contribution from land-based biomass combustion. This result confirms the previous interpretation based on the Fl/Pyr ratio (Table 3.3). Despite the presence of steel, iron and aluminum industries in the surrounding area (<50 km), no B[a]Ant/Σ228 value over 0.8, which is characteristic of coal or smelters, was observed. In addition, in many studies, indeno[1,2,3-cd]pyrene and benzo[ghi]-perylene have been used as markers of automobile emissions (Hartmann *et al* 2004 ; Harkov *et al* 1984). In this study, the absolute concentrations of benzo[ghi]perylene and indeno[1,2,3-cd]pyrene were important, ranging from 30 to 1,070 µg.kg^{-1} and from 26 to 662 µg.kg^{-1}, respectively. Indeed, a plot of IP/Σ276, which is (IP + B[ghi]P), revealed a signature ratio found between 0.6 and 0.8, indicating biogenic combustion (P1–P12).

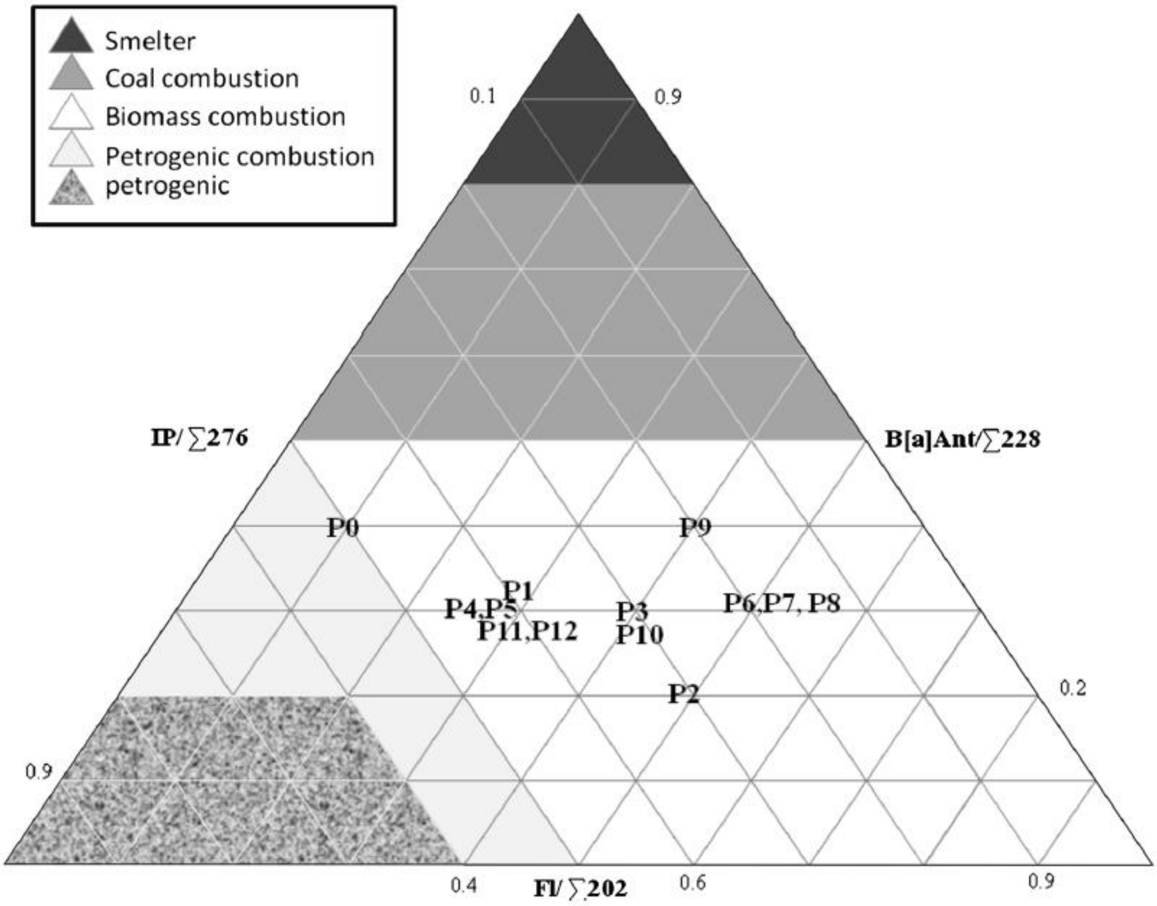


Figure 3.4. Ternary diagram differentiation of PAH origin using a plot of Fl/Σ202, B[a]Ant/Σ228 and of IP/(IP + B[ghi]P). The respective ratios were normalized.

3.3.3. LABs

During industrial sulfonation processes for LAS synthesis, 1–3 % of LABs remain unreacted (Gledhill *et al* 1991). Thus, LABs are considered to be tracer residues for cleaners and detergents in the environment; in addition, they have been proposed as molecular tracers for wastewater entering coastal marine environments wherever LABs are being used and released (Gustafsson *et al* 2001). The concentrations of the total LABs (in µg.kg^{-1}) measured at each sampling point are shown in Table 4. Typical chromatograms simplified structure of LABs is presented in Fig. 3.3b. No mass spectrometric interference with tetrapropylene-based alkyl benzenes (m/z = 105 and 119) has been recorded for LABs (m/z = 91 and 105) (Eganhouse and Pontolillo, 2008). Table 3.4 shows LAB levels in Cortiou sediments ranging from 42.9 to 502.3 µg.kg^{-1}. Compared to levels found in many developed countries with WWTPs, the concentrations of total LABs found in this study are rather low. For instance, Murray *et al* (1987) showed that LABs in Australian coastal sediments ranged from 10 to 19,400 µg.kg^{-1}. Extremely high concentrations of over 10,000 µg.kg^{-1} were observed in sediments from Jakarta, Indonesia (Isobe *et al* 2004), and were attributed to the absence of WWTPs. Three LAB homologs were found in Cortiou sediments, with 11 different resolved isomers (Table 3.4). Technical formulations of commercial detergents contain 10–15, 25–35, 25–35, 15–30 and 0–5 % of C_{10}, C_{11}, C_{12}, C_{13} and C_{14} homologs, respectively (Cavalli *et al* 1993). Furthermore, in Europe, more than 98 % of C_{10}–C_{13} homolog LABs are used as the main components of commercial detergent formulations, predominantly containing C_{11} and C_{12} (Hera 2007; Gordon *et al* 2009). We observed higher concentrations of linear alkyl benzenes with 12 carbon atoms (C_{12}-LAB), followed by C_{10}-LAB and C_{11}-LAB, accounting for an average of 44.9, 28.3 and 26.7 % of the total LABs, respectively. The linear alkyl chains typically have 10–13 carbon units, with approximate ratios of $C_{10}/C_{11}/C_{12}/C_{13}$ being 3/30/33/24, with an average carbon number near 11.6 (Cavalli *et al* 1993; Viguri *et al* 2002; Hera 2007). LAS environmental fingerprints previously detected in aquatic environmental samples contained $C_{10}/C_{11}/C_{12}/C_{13}$ at 45:30:23:2 with an average carbon number of 10.8 (Cavalli *et al* 1993). In this study, a ratio of $C_{10}/C_{11}/C_{12}/C_{13}$ of 25.1/25.4/45.5/0 was observed, with an average carbon number of 11.2. The predominance of C_{12}-LAB in this study was in agreement with the finding of the previous study (Gustafsson *et al* 2001; Rico-Rico *et al* 2009). The predominance of C_{12}-LAB (34 %) has also been reported by Eganhouse and Sherblom (2001) in municipal WWTP discharge combined with sewer effluents near Boston Harbor. Furthermore, as shown in Table 3.4, the overall values reveal a removal of odd-numbered alkyl chain LABs. For instance, only traces of C_{13} LABs under the quantitation limit were detected. The absence of C_{13}-LABs and the slight reduction in the C_{11}-LAB proportion might be due to a selective microbial degradation of the odd-numbered alkyl chain homolog. A supporting argument for such condition is that LABs biodegradation is initiated by an x-oxidation of the alkyl chain followed by successive cleavage of C_2 fragments (b-oxidation), facilitating microbial attack on odd-numbered alkyl chains (Hera 2007). For C_{13}-LAB, such an occurrence is consistent with previous studies, which have demonstrated that the long-chain LABs are more susceptible to biodegradation than the shorter ones (Eganhouse and Sherblom 2001; Eganhouse and Pontolillo 2008).

Table 3.4. Identification and quantification of LABs in Cortiou sediments (µg.kg^{-1})

LAB	P0	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	Average P1 - P12
5-C_{10}-LAB	4.9	7.7	6.4	11.8	67.7	32.1	39.4	28	24.4	0	1.8	3.3	12.3	19.6
4-C_{10}-LAB	6.4	3.8	3.1	6.2	27.5	12.6	14.1	14.8	2.6	7.9	0.9	1.9	6.3	8.5
3-C_{10}-LAB	4.3	2.7	1.9	4.7	16.4	8.5	7.7	6.3	2.2	4.8	0.7	1.5	4.5	5.2
2-C_{10}-LAB	7.8	9.4	7.6	15	62.9	44	59	4.1	1.3	3.5	3.8	5.2	13.9	19.1
5-C_{11}-LAB	14.2	11.1	8.3	17.4	64.8	43.6	55.4	16.9	4.7	14.3	4.1	6.4	15.3	21.9
4-C_{11}-LAB	12.3	7.1	5.4	12	38.3	26.1	30.6	17.5	3.6	15	2.8	4.4	11	14.5
2-C_{11}-LAB	9.2	5.7	4.1	9	21.9	13.9	14.1	9.8	2.6	11	2.1	3.2	23.4	10.1
5-C_{12}-LAB	13.5	18	15.1	28.7	85.8	67.3	85.3	3	0.6	3.6	10.1	11.5	15.4	28.7
4-C_{12}-LAB	22.8	11.8	9.6	19.2	50.4	39.7	47.9	32.5	9.4	30	6.8	7.9	11.7	23.1
3-C_{12}-LAB	14.3	9.1	6.9	14.7	33.3	26.6	30	17.2	4.8	16.7	5.5	6.1	2	14.4
2-C_{12}-LAB	6.1	7.6	5.2	14.3	33.3	26.6	12	3	0.7	0	4.4	5.9	8.7	10.1
ΣLAB	115.8	94.1	73.6	153.4	502.3	341,1	395.6	153	56.9	106.8	42.9	57.3	124.2	175.1
I/E*	0.31	0.63	0.7	0.59	0.73	0.72	0.95	0.06	0.04	0.08	0.6	0.58	0.7	0.53

*I/E = P(6-, 5-C_{12} AB) P (4-, 3-, 2-C_{12} AB). LAB = Linear alkyl benzene

LABs are manufactured in large-scale industrial processes by alkylating benzene with linear mono-olefins or alkyl halides such as chloroparaffins using HF or $AlCl_3$ as the alkylation catalyst, with average proportions of the homolog isomers 2-, 3-, 4-, 5- and 6-phenyl of 23, 17.5, 17, 21 and 21.5 %, respectively (Cavalli *et al* 1993). This study found a C12 isomer distribution of 28.7, 23.1, 14.4 and 10.1 % (by weight) for the 5-, 4-, 3- and 2-C_{12}, respectively (Table 3.4). The presence of nC_{12} isomers was confirmed based on the occurrence of diagnostic ions (at m/z 91 + (n 9 14) and 91 + ((m–n) 9 14)). The absence of the 6-C_{12} isomer, which has not been previously reported, is most likely a consequence of biodegradation processes that are faster for homologs having an m number of twice their n number (such as 6-C_{12}-LAB). Calculation of the ratios between the internal (I) and external (E) isomers of LABs is useful (Bayona *et al* 1986). External isomers are defined as isomers whose phenyl substitution positions are near the terminal end of the alkyl chain. External isomers (phenyl in position 2, 3 or 4 on the alkyl chain) are more susceptible to microbial attack than internal isomers (Eganhouse and Sherblom 2001). Therefore, the I/E ratio is proposed by some authors to be an indicator of the extent of LAB degradation (Bayona *et al* 1986; Gustafsson *et al* 2001; Gordon *et al* 2009). In this study, I/E values varied from 0.04 to 0.73 with an arithmetic mean of 0.53, while I/E for P0 was about 0.31 (Table 3.4). Thus, few external isomers of the LAB were degraded, indicating incomplete degradation performance in the WWTP. Gustafsson *et al* (2001) found that I/E ratios decreased with increasing distance from the source (~6) to offshore (< 1) in Boston Harbor. Luo *et al* (2008) found that I/E ratios in sediments collected far away from the source were lower than those in sediments collected in a coastal area adjacent to the source. In this work, samples collected at stations P7–9 had lower I/E ratios. Such ratio value can be explained by WWTP discharges containing high organic material, leading to a faster burial of LABs (K_{ow} ranged from 7.45 to 8.19) and thereby reducing the relative importance of aerobic degradation. Alternatively, anaerobic degradation may occur, resulting in no change in I/E ratios (Viguri *et al* 2002). Even there is an improvement of the low I/E ratios in the Cortiou sediments (average for P1–P12 was 0.53) compared to P0 (0.31) (Table 3.4) ; the findings, however, cannot determine whether the remaining LABs consisted of partially transformed degradation products (i.e., intermediates that could not have been used as carbon sources by the microorganisms present) or remaining LAB homologs that could not be transformed by the microbial population. In this sense, some environmental processes might change I/E ratios during transport when we compared low I/E ratios in the WWTP sewerage canal and slight improvement seaward (P1–P12). In a partial conclusion, the present study demonstrated the usefulness of I/E ratio to evaluate the effectiveness of sewage treatment systems showing by the lower value of I/E at P0 but application of such ratios to the other transitional area should be applied with caution because of its complexity interaction i.e., biotic and abiotic factors.

3.3.4. Correlation with organic matter

Total carbon and TOC were measured in the Cortiou sediments. TC varied from 0.072 to 0.129 mg C. mg^{-1} sediment, and TOC ranged from 0.005 to 0.089 mg.C.mg^{-1} sediment. TOC represented 6.2 – 68.7 % of TC. The analysis of variance (ANOVA) and linear regression were employed to compare differences in Σ n-alkane, ΣPAHs and ΣLABs with the physicochemical properties (EOM, TC and TOC) in the surface sediments of Cortiou and to explore correlations between those parameters (Table 3.3).

The regression analysis exhibited that the sum PAHs concentration had significant correlations with MOE and TOC in surface sediments (p 0.05, n = 13), while the total 16 priority PAHs did not show any statistically significant correlations with TC properties of the surface sediments (Table 3.5). Our finding is in accordance with the previous studies that demonstrated good linear relationships between total PAHs and organic matter content in surface sediments (Viguri *et al* 2002; Wang *et al* 2011), but in contrary with Hung *et al* (2010, 2011) who argued that PAHs can more easily be affected by black carbon as compared to organic matter. Despite the fact that study area is also affected by repeated fires (Vergnoux *et al* 2011), the sedimentary PAHs in the study area are not exclusively pyrolytic, and association of soot carbon (as part of TC) with planar surface of polyaromatic soot might be lower (Hung *et al* 2010). Interestingly, the n-alkanes and LABs showed the opposite, correlating with TC significantly stronger than PAHs. A possible explanation is that the distribution of n-alkanes and LABs in the surface sediments might relate to input sources (biogenic terrestrial) reflecting by TC (i.e., soot carbon) rather than bulk organic sediment. Therefore, this finding suggests that these three classes of pollutants might not be derived from the same source. The poor correlations between target pollutants and the sediment properties were not expected. P7–P9 had higher TOC levels (4.9–8.8 %) than those in other sites close to Cortiou (0.5–3.1 %). Disregarding data from P7 to P9 resulted in better correlations between pollutants and the sediment properties (MOE, TC and TOC). From Electronic Supplementary Material, Fig. A, we can observe a zone highly perturbed in the 600–800 m from coastal (corresponds to P7–P9).

Table 3.5. Adjusted determination coefficient *(r^2)* for categorical compounds (n-alkanes, PAHs and LABs) with MOE, TC and TOC in Cortiou sediments.

	MOE			**TC**			**TOC**		
	F	**P**	**Adjusted r^2**	**F**	**P**	**Adjusted r^2**	**F**	**P**	**Adjusted r^2**
Σn-alkanes	0.0138	0.904	0	2.785	0.123	**0.129**	0.0611	0.809	0
ΣLAB	0.0009	0.977	0	1.565	0.237	**0.045**	0.0163	0.901	0
ΣPAHs	6.442	0.028	**0.312**	0.28	0.607	0	2.798	0.123	**0.13**
Calculation without taking into account the data from P7 - P9									
Σn-alkanes	3	0.145	**0.151**	2.779	0.134	**0.165**	9.076	0.017	**0.473**
ΣLAB	21	0.002	**0.694**	0.567	0.473	0	14.235	0.005	**0.596**
ΣPAHs	7.49	0.026	**0.419**	0.157	0.702	0	16.551	0.004	**0.633**

Bold character was regarded as being significant for all the tests
PAH polycyclic aromatic hydrocarbons, LABs linear alkyl benzenes, MOE material organic extractable, TC total carbon, TOC total organic carbon.

Moreover, Vousdoukas *et al* 2011 deployed oceanographical data collection system in this area for a period of 2–3 months and recorded several suspension and erosion events that have been identified when significant wave heights exceeding 1.5 m. Due to their hydrophobicity, n-alkanes and LABs are expected to have positive correlations with organic matter content. For instance, when the data for P7–P9 were excluded, the adjusted determination coefficients of MOE correlate significantly with Σn-alkanes, ΣLABs and total ΣPAHs by value 0.151, 0.694 and 0.419, respectively. More robust relationships were observed for Σn-alkanes, ΣLABs and ΣPAHs with TOC showing the value 0.473, 0.596 and 0.6333, respectively. Regarding the TC, only the Σn-alkanes exhibit significant correlations, confirming sources input hypothesis. Accordingly, P7–P9 might correspond to a hydrodynamically disturbed zone related to the mixing processes of the two different water masses. Hung *et al* 2007 found similar distribution for different persistent organic pollutants in the Danshui River estuary and adjacent coastal area in Taiwan. In fact, as suggested by Hung *et al* 2006, such random distribution may be due to irregular riverine input or wastewater plant discharge; tidal amplitude or residence times of the coastal water may affect these pollutant distributions rather than the source input, excepted for the n-alkanes in our case.

3.3.5. Environmental significance

Due to their bioaccumulation and biomagnification potentials, the occurrence and fate of sedimentary hydrocarbons in the environment is of particular interest. Generally, n-alkanes are not of much toxicological concern and are not reported to possess carcinogenic, teratogenic or mutagenic properties (Bellas *et al* 2011). No information is available to date for n-alkane sediment quality standard criteria and benchmarks related to protection of aquatic biota. PAHs, however, are described as toxic, and some aromatics are potentially carcinogenic (Long and Morgan 1990). The effects of range-low (ERL) values (Burton *et al* 2002) were considered in evaluating the possible ecotoxicological risks of PAHs in the study area. The measured concentrations of PAHs were then compared with their ERL levels. More than 40% of stations (P2–P7) exhibited contamination levels higher than ERL values (3,500 µg.kg^{-1}), indicating an 85 % likelihood that sediment will cause an adverse effect to the sedimentary biota. Threshold effect level (TEL) values represent the concentrations below which adverse effects are expected to occur only rarely for PAHs in sediments. The remaining 60 % stations exceeded the TEL value of 870 µg.kg^{-1} (Peters *et al* 1999). Levels in sediments collected at stations P1 and P9–P12 ranged between the TEL and ERL benchmarks, suggesting probable adverse effects. Peters et al. (1999) noted that benzo[a]pyrene is used to assess the toxicities of other PAHs expressed as toxic equivalency factors (TEFs). According to the US Environmental Protection Agency (US EPA 1993), TEFs for benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene are 0.1, 1, 0.1, 0.01, 0.1 and 1, respectively. Sprovieri *et al* (2007) proposed total concentrations of potentially carcinogenic PAHs (CPAHs), which consist of benzo[a]anthracenes, benzofluoranthenes, benzo[a]pyrenes, indeno[1,2,3-cd]pyrenes and dibenzo[a,h]anthracenes. The values varied from 163 to 3,801 µg.kg^{-1} and accounted for 20–60 % of PAHs in sediments from Cortiou (Table 3.3). The unreacted residual LABs are discharged to coastal areas almost exclusively from sewage outfalls and are considered reliable sewage tracers (Peters *et al* 1999). Following exposure assessments, the environmental risk characterizations of LABs for biota in the aquatic, terrestrial and soil categories were extensively evaluated by the European Council for Commission Regulation (EC) 1488/94. The report concluded that there are no concerns today for the environment or human health.

3.4. Conclusion

The calculated hydrocarbon indexes suggest that terrestrial biogenic inputs are the main sources of n-alkanes while pyrolytic sources derived from wood and biomass combustion contribute to the PAHs in surface sediments with the exception for P0, which can be origin of petrogenic. High hydrocarbon levels were generally found in the areas associated with high human impacts and harbor activities in the bay. LABs, which were used as a tracer of anthropogenic pollution in Cortiou sediments, were detected at the whole sampling locations. P0 I/E ratio (the ratios of internal isomers to external isomers in LABs) was low, suggesting that inadequately treated sewage is discharged into the marine environment. More after, low I/E ratios followed by C_{13}-LABs and 6-C_{12}-LABs in sediments with high total LAB concentrations suggest that a biodegradation process may take place concomitantly with a continually heavy load of untreated sewage. Thus, regular monitoring of LABs could provide an effective tool to assess the effectiveness of the implementation of sewage treatment systems. The high contaminant levels followed by a cumulative concentration of several toxic compounds may increase overall sediment toxicity. Thus, these findings highlight the necessity of continued environmental monitoring to assess sewage pollution release in coastal areas and determine the level of improvement of one of the‘‘biggest’’ WWTPs in the world (Géolide). It is necessary to avoid future contaminant discharge into the National Park to ensure a better marine environment.

Acknowledgments This work was supported by the ANR project MARSECO (2008 CESA 018) in the framework of the research federation ECCOREV. The authors express their gratitude to the anonymous referees for their constructive comments. We are grateful to De F. Valroger and D. Eric for assistance with diving for sediment sampling and to N. Marriner for assessing English revisions. We also thank M. Bresson and J. F. Barbion for their assistance during sampling trips. The first author acknowledges Grants-in-Aid from the National Ministry of Education of Indonesia (DIKTI and BPKLN Kemdiknas Grants).

References

Asia L, Mazouz S, Guiliano M, Doumenq P, Mille G (2009) Occurrence and distribution of hydrocarbons in surface sediments from Marseille Bay (France). Mar Pollut Bull 58:424–455.

Baumard P, Budzinski H, Garrigues P (1998) Polycyclic aromatic hydrocarbons (PAHs) in sediments and mussels of the western Mediterranean Sea. Environ Toxicol Chem 17:765–776.

Bayona JM, Albaiges J, Solanas AM, Grifoll M (1986) Selective aerobic degradation of linear alkylbenzenes by pure microbial cultures. Chemosphere 15:595–598.

Bellas J, Nieto O, Beiras R (2011) Integrative assessment of coastal pollution: development and evaluation of sediment quality criteria from chemical contamination and ecotoxicological data. Cont Shelf Res 31:448–456.

Benner R, Strom M (1993) A critical evaluation of the analytical blank associated with DOC measurements by high-temperature catalytic oxidation. Mar Chem 41:153–160.

Blumer M (1957) Removal of elemental sulfur from hydrocarbon fractions. Anal Chem 29:1039–1041.

Bourbonniere RA, Meyers PA (1996) Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. Limnol Oceanogr 41:352–359.

Budzinski H, Jones I, Bellocq J, Pie´rard C, Garrigues P (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Mar Chem 58:85–97.

Burton GA Jr, Batley GE, Chapman PM, Forbes VE, Smith EP, Reynoldson T, Schlekat CE, den Besten PJ, Bailer AJ, Green AS, Dwyer RL (2002) A weight-of-evidence framework for assessing sediment (or other) contamination: improving certainty in the decision-making process. Hum Ecol Risk Assess 8:1675–1696.

Cavalli L, Gellera A, Landone A (1993) LAS removal and biodegradation in a wastewater treatment plant. Environ Toxicol Chem 12:1777–1788.

Deng W, Li CG, Li SY, Ma YY, Zhang DH (2013) Source apportionment of polycyclic aromatic hydrocarbons in surface sediment of mud areas in the East China Sea using diagnostic ratios and factor analysis. Mar Pollut Bull 70:266–273.

Eganhouse RP, Pontolillo J (2008) Susceptibility of synthetic longchain alkylbenzenes to degradation in reducing marine sediments. Environ Sci Technol 42:6361–6368.

Eganhouse RP, Sherblom PM (2001) Anthropogenic organic contaminant in the effluent of a combined sewer overflow: impact on Boston Harbor. Mar Environ Res 51:51–74.

Fromme H, Lahrz T, Piloty M, Gebhardt H (2004) Polycyclic aromatic hydrocarbons inside and outside of apartments in an urban area. Sci Total Environ 326:143–149.

Gledhill W, Saeger VW, Trehy ML (1991) An aquatic environmental safety assessment of linear alkylbenzene. Environ Toxicol Chem 10:169–178.

Gordon AK, Muller WJ, Gysman N, Marshall SJ, Sparham CJ, O'Connor SM, Whelan MJ (2009) Effect of laundry activities on in-stream concentrations of linear alkylbenzene sulfonate in a small rural South African river. Sci Total Environ 407:4465–4471.

Gustafsson O, Long CM, Macfarlane J, Gschwend PM (2001) Fate of linear alkylbenzenes released to the coastal environment near Boston Harbor. Environ Sci Technol 35:2040–2048.

Harkov R, Kebbekus B, Bozzelli JW, Lioy PJ, Daisey J (1984) Comparison of selected volatile organic compounds during the summer and winter at urban sites in New Jersey. Sci Total. Environ 38:259–274.

Hartmann PC, Quinn JG, Cairns RW, King JW (2004) The distribution and sources of polycyclic aromatic hydrocarbons in Narragansett Bay surface sediments. Mar Pollut Bull 48:351–358.

HERA (2007) HERA-LAS Human and Environmental Risk Assessment: Linear Alkylbenzene Sulphonates. LAS. CAS No. 68411-30-3, Version 3.0, Oct 2007. http://www.heraproject.com.

Hinga KR (2003) Degradation rates of low molecular weight PAH correlate with sediment TOC in marine subtidal sediments. Mar Pollut Bull 46:466–474.

Hung CC, Gong GC, Jiann KT, Yeager KM, Santschi PH, Wade TL, Sericano JL, Hsieh HL (2006) Relationship between carbonaceous materials and polychlorinated biphenyls (PCBs) in the sediments of the Danshui River and adjacent coastal areas, Taiwan. Chemosphere 65:1452–1461.

Hung CC, Gong GC, Chen HY, Hsieh HL, Santschi PH, Wade TL, Sericano JL (2007) Relationships between pesticides and organic carbon fractions in sediments of the Danshui River estuary and adjacent coastal areas of Taiwan. Environ Pollut 148:546–554.

Hung CC, Gong GC, Ko FC, Chen HY, Hsu ML, Wu JM, Peng SC, Nan FH, Yeager KM, Santschi PH (2010) Relationships between persistent organic pollutants and carbonaceous materials in aquatic sediments of Taiwan. Mar Pollut Bull 60:1010–1017.

Hung CC, Gong GC, Ko FC, Lee HY, Chen HY, Wu JM, Hsu ML, Peng SC, Nan FH, Santschi PH (2011) Polycyclic aromatic hydrocarbons in surface sediments of the East China Sea and their relationship with carbonaceous materials. Mar Pollut Bull 63:464–470.

Inengite AK, Oforka NC, Leo CO (2013) Source identification of polycyclic aromatic hydrocarbons in sediments of a creek around a flow station. Int J Environ Sci Technol 10(3):519–532.

Ishiwatari R, Takada H, Yun SJ, Matsumoto E (1983) Alkylbenzene pollution of Tokyo Bay sediments. Nature 301:599–600.

Isobe KO, Zakaria MP, Chiem NH, Minh LY, Prudente M, Boonyatumanond R, Saha M, Sarkar S, Takada H (2004). Distribution of linear alkylbenzenes (LABs) in riverine and coastal environments in South and Southeast Asia. Water Res 38:2449–2459.

Jeng WL (2006) Higher plant n-alkane average chain length as an indicator of petrogenic hydrocarbon contamination in marine sediments. Mar Chem 102:242–251.

Kanzari F, Syakti AD, Asia L, Malleret L, Mille G, Jamoussi B, Abdelrrabba M, Doumenq P (2012) Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), organochlorine and organophosphorous pesticides in surface sediments from the Arc River and the Berre Lagoon, France. Environ Sci Pollut Res 19(2):559–576.

Léon VM, Gonzalez-Mazo E, Gomez-Parra A (2000) Handling of marine and estuarine samples for the determination of linear alkylbenzene sulfonates and sulfophenylcarboxylic acids. J Chromatogr A 889:211–219.

Liu X, Jia H, Wang L, Qi H, Ma W, Hong W, Guo J, Yang M, Sun Y, Li YF (2013) Characterization of polycyclic aromatic hydrocarbons in concurrently monitored surface seawater and sediment along Dalian coast after oil spill. Ecotoxicol Environ Saf 90:151–156.

Long ER, Morgan LG (1990) The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. NOAA Office of Oceanography and Marine Assessment, Seattle, WA, p 220.

Luo XJ, Chen SJ, Ni HG, Yu M, Mai BX (2008) Tracing sewage pollution in the Pearl River Delta and its adjacent coastal area of South China Sea using linear alkylbenzenes (LABs). Mar Pollut Bull 56:158–162.

Micic V, Kruge M, Komer P, Bujalski N, Hofmann T (2010) Organic geochemistry of Danube River sediments from Pancˇevo (Serbia) to the Iron Gate dam (Serbia–Romania). Org Geochem 41:971–974.

Mille G, Asia L, Guiliano M, Malleret L, Doumenq P (2007) Hydrocarbons in coastal sediments from the Mediterranean sea (Gulf of Fos area, France). Mar Pollut Bull 54:566–575.

Mungray AK, Kumar P (2009) Fate of linear alkylbenzene sulfonates in the environment: a review. Int Biodeterior Biodegradation 63:981–987.

Murray AP, Gibbs CF, Kavanagh PE (1987) Linear alkylbenzenes (LABs) in sediments of Port Phillip Bay (Australia). Mar Environ Res 23:65–76.

Olivella MA, Ribalta TG, de Febrer AR, Mollet JM, de Las Heras FX (2006) Distribution of polycyclic aromatic hydrocarbons in riverine waters after Mediterranean forest fires. Sci Total Environ 355:156–166 Page.

DS, Boehm PD, Douglas GS, Bence AE, Burns WA, Mankiewicz PJ (1999) Pyrogenic polycyclic aromatic hydrocarbons in sediments record past human activity: a case study in Prince William Sound, Alaska. Mar Pollut Bull 38:247–260.

Peters CA, Knightes KD, Brown DG (1999) Long-term composition dynamics of PAH-containing NAPLs and implications for risk assessment. Environ Sci Technol 33:4499–4507.

Rico-Rico A, Temara A, Behrends T, Hermens JLM (2009) Effect of sediment properties on the sorption of C12-2-LAS in marine and estuarine sediments original. Environ Pollut 157:377–383.

Schutzendubel A, Majcherczyk A, Johannes C, Hu¨ttermann A (1999). Degradation of fluorene, anthracene, phenanthrene, fluoranthene, and pyrene lacks connection to the production of extracellular enzymes by Pleurotus ostreatus and Bjerkandera adusta. Int Biodeterior Biodegradation 43:93–100.

Sikes EL, Uhle ME, Nodder SD, Howard ME (2009) Sources of organic matter in a coastal marine environment: evidence from n-alkanes and their d13C distributions in the Hauraki Gulf, New Zealand. Mar Chem 113:149–163.

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

Syakti AD, Hidayati NV, Hilmi E, Piram A, Doumenq P (2013) Source apportionment of sedimentary hydrocarbons in the Segara Anakan Nature Reserve, Indonesia. Mar Pollut Bull 74:141–148.

Tao S, Li X, Yang Y Jr, Coveney RM, Lu X, Chen H, Shen W (2006) Dispersion modeling of polycyclic aromatic hydrocarbons from combustion of biomass and fossil fuels and production of coke in Tianjin, China. Environ Sci Technol 40:4586–4591.

Tao S, Liu YN, Xu W, Lang C, Liu SZ, Dou H, Liu WX (2007) Calibration of a passive sampler for both gaseous and particulate phase polycyclic aromatic hydrocarbons. Environ Sci Technol 41:568–573.

US Environmental Protection Agency (US EPA) (1993) Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPAy600yRy089. Office of Research and Development, US EPA, Washington, DC.

Vergnoux A, Malleret L, Asia L, Doumenq P, Theraulaz F (2011) Impact of forest fires on PAH level and distribution in soils. Environ Res 111:193–198.

Viguri J, Verde J, Irabien A (2002) Environmental assessment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Santander Bay, Northern Spain. Chemosphere 48:157–165.

Volkman JK, Revill AT, Holdsworth DG, Frederick D (2008) Organic matter sources in an enclosed coastal inlet assessed using lipid biomarkers and stable isotopes. Org Geochem 39:689–710.

Vousdoukas MI, Verney R, Dufois F, Pinazo C, Sauzade D, Meule S, Cann P, Plomaritis TA (2011) Sediment dynamics in the Bay of Marseille, Gulf of Lions (France): hydrodynamic Forcing vs.Bed Erodibility. J Coast Res 27:942–958.

Wagener ALR, Meniconi MFG, Hamacher C, Farias CO, da Silva GC, Gabardo IT, Scofield AL (2012) Hydrocarbons in sediments of a chronically contaminated bay: the challenge of source assignment. Mar Pollut Bull 64:284–294.

Wang XC, Zhang YX, Chen RF (2011) Distribution and partitioning of polyaromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. Mar Pollut Bull 42:1139–1149.

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios indicators of PAH source and composition. Org Geochem 33:489–515

CHAPTER IV

DISTRIBUTION OF ORGANOCHLORINE PESTICIDES (OCs) AND POLYCHLORINATED BIPHENYLS (PCBs) IN MARINE SEDIMENTS DIRECTLY EXPOSED TO WASTEWATER FROM CORTIOU, MARSEILLES

Agung Damar SYAKTI, Laurence ASIA, Fehmi KANZARI, **Halikuddin UMSANGAJI**, Laure MALLERET, Yann TERNOIS, Gilbert MILLE, Pierre DOUMENQ

SUMMARY

Pesticides are the substances of organic chemistry which existed since ancient Greece, including the use of sulfur. Thanks to their capacity to protect cultivated plants and harvested products, 95% of these substances are used in agriculture. Beside, these substances also have toxic or even lethal properties towards humans (Solomon *et al* 2000; Tron *et al* 2001; Meeker *et al* 2006a,b). The most affected population is that of farmers who are directly exposed to this type of pollution, with the appearance of respiratory diseases (asthma, respiratory failure), cancers (testicles, cerebral, lymphoma, etc.) or neurological diseases. degenerative diseases such as Parkinson's or Alzheimer's disease (Baldi *et al* 2001; Ascherio *et al* 2006).

Furthermore, in the following part of our study, we will also present the compounds derive from urban and industrial activities discharges, namely PCBs. These substances are found especially in electrical transformers and capacitors, but also in heat transfer fluids, in additives to paints or in plastics and inks. Brunet and Rocher (2000) showed that PCBs are also endocrine disruptors because they affect reproduction in some animals by causing abortions. Some PCBs are also immunosuppressive and are classified as probably carcinogenic and mutagenic agents for humans (Brunet 2007). The method used in this work was carried out by the extraction of solvents with soxtherm and the chromatographic colons were used for the separation of the substances, whereas the identification was employed GC-MS. This work was carried out in the framework of French National Research MARSECO which we observed the existence of OCs and PCBs in marine sediments and their recent potential for contamination through pollution indices and potential environmental risk. There was several works on the existence of these compounds in the marine environment but they are not taken into account specifically about the behaviors of these substances at the level of physical factors and plume dynamics. The results obtained also enabled to compare the concentration levels with some previous works.

Concerning the OCs, the first result presents on the spatial distribution of these substances through the plume vary from 1.20 $\mu g.kg^{-1}$ to 190.60 $\mu g.kg^{-1}$ with the average value of 89.58 $\mu g.kg^{-1}$ which was dominated by pp'DDD and endosulfan sulfat. This distribution describes the highest concentrations found at the nearest stations of WWTPs outfall and decreases moderately at P2 and P3. Nevertheless, they re-increase at the P4 and P5 stations. Then the levels of pesticide OCs were diluted at the offshore stations. Through the statistical analysis, we observed that there was no correlation between the abundance of OCs and the presence of TOC. This implied that there were other factors that control the sorption of these substances in sediments. It is probably other local factors such as meteorological aspects that play an important role on these processes. The most interesting of our results is the higher concentrations of these substances to the east of plume compared to those in the west. As our previous explanation that this mode related to the phenomenon of plume deviation whose predominant to eastwards under the influence of wind direction. According to the sediment quality assessment in our work, we found that some sediments in Cortiou are probably associated with toxic effects particularly OCs pesticides.

Second results we present in this chapter is the occurrence of PCBs and their spatial distribution through the plume close to the emissary point of WWTPs. The dissemination of these chemicals vary between 11.50 $\mu g.kg^{-1}$ and 791.50 $\mu g.kg^{-1}$ with the average value of 293.51 $\mu g.kg^{-1}$, whose predominant congeners are CB-138 and CB -153. Moreover, the highest concentrations are found in the nearest stations at the point of emissary except station P1. Then they decrease at the plume centers and re-increase at the offshore stations. This proves that these PCBs are able to move further away.

This article was published in the journal " Environmental Pollution and Science Research " as part of this work (2011).

According to the assessment of sediment quality at 12 stations in Cortiou suggested that 50% of this study sites are contaminated by PCBs and those that remain are heavily contaminated especially P2, P3, P4, P5 which were found near point of emissary and P7, P8 which were detected at the offshore area.

DISTRIBUTION OF ORGANOCHLORINE PESTICIDES (OCs) AND POLYCHLORINATED BIPHENYLS (PCBs) IN MARINE SEDIMENTS DIRECTLY EXPOSED TO WASTEWATER FROM CORTIOU, MARSEILLES

Agung Damar SYAKTI, Laurence ASIA, Fehmi KANZARI, **Halikuddin UMSANGAJI**, Laure MALLERET,
Yann TERNOIS, Gilbert MILLE, Pierre DOUMENQ

Abstract

Introduction The future 'Calanque National Park' coastlines of the Bouches-du-Rhône and Var departments in France, constitute one of the ten biodiversity hot spots identified in the Mediterranean basin that receives industrial and urban wastewaters discharged from Marseille and its suburbs.

Materials and methods Organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) were measured in sediments collected from 12 sampling sites (C1–C12) of sewage discharge to the sea from the wastewater treatment plant of Cortiou-Marseille. This study aims to determine the extent of these compounds in the sediments and to establish the possible sources of these contaminants.

Results and discussion Total pesticides in the sediments ranged from 1.2 to 190.6 ng.g^{-1} dry weight of sediment. The highest value was found at station C1, with a decreasing trend in total OC concentrations seaward. Among these compounds, the concentrations of the sum of dichlorodiphenyltrichloroethane (ΣDDT) were the highest, ranging from 0.7 to 114.3 ng g^{-1}. PCB concentrations, expressed as equivalent to Arochlor 1260, varied from 9.1 to 226.9 ng.g^{-1}. Individually, the dominant coplanar PCB congeners CB-153, CB-138 and CB-101. Generally, PCB concentrations at stations C2, C3, C5 and C7 were higher than those at stations C10, C11 and C12. Through some pollution indices, we showed the long-term contamination input of these OCs (DDT, endosulfan, HCH and heptachlor cases) rather than a recent release resulting from degradation and long-term weathering (dieldrin, aldrin and methoxychlor cases). Occurrence of PCBs might be due to their resistance to degradation processes or/and chronic inputs.

Conclusions
By comparison with available sediment quality guideline (SQG) values, the environmental significance and toxicological implications of PCBs and OCs (i) reveal the probable adverse effects for the sediments from C1, C5, C6, C9 and (ii) confirm the adverse effect for marine biota and more particularly for benthic communities at C2–C4, C7 and C8.

Keywords : Persistent organic pollutants . Chlorinated pesticides . PCBs . Environmental monitoring . National Park .Wastewater treatment plan discharge

4.1. Background, aims and scope

The coastlines of the Bouches-du-Rhône and Var departments in France, and more specifically the Calanque massif, are recognized for their rich biodiversity and environmental significance (Aboucaya *et al* 2001). This biogeographical region constitutes one of the ten biodiversity hot spots identified in the Mediterranean basin (Médailand Quézel 1997). In order to better mitigate, protect and conserve against human impact, the creation of the Calanque National Park' has been proposed and iscurrently under legislative review. Our study site is located in the center of the future 'Calanque National Park', where the potential pollutants of the marine environment primarily derive from treated urban wastewater discharged at a rate of up to 280,000 m^3 each day. This includes used water from Marseille and its suburbs, a population of at least 1.8 million people. Other potential persistent organic pollutants (POPs) derived from Marseille and the Huveaune River, particularly during intense rainfall, can be bypassed through the Cortiou messenger. In 2008, Marseille's authorities upgraded their wastewater treatment plan 'Géolide' by integrating a biological treatment which considerably reduced the impact of urban organic pollutants on the marine environment but did not entirely resolve the problem of some POPs such as organochlorine pesticides (OCs) and polychorinated biphenyls (PCBs) released by daily urban activities. Due to their impact on nontarget organisms and biological accumulation via the food chain, as well as their affinity towards natural organic matter, OCs and PCBs are known for their toxicity and environmental persistency (Agency for Toxic Substances and Disease Registry (ATSDR) 2007). Furthermore, the Stockholm Convention on Persistent Organic Pollutants in 2001 (United Nations Environment Program (UNEP 2006) and the European Regulation 850/2004/EC (2004) registered most of these substances on a priority list of pollutants. Despite their ban during the early 1980s, and National Implementation Plans developed by Stockholm's signatory countries, many studies have shown the residual distribution of these compounds (Liu *et al* 2007) in sediments (El-Kady *et al* 2007), water (Carvalho *et al* 2009), biota (Magnusson *et al* 2006) and aerosols (Mandalakis *et al* 2002) or even recent use through different formulations (Kim *et al* 2004). Moreover, the accumulation of OCs and PCBs in sediments and aquatic organisms, such as fish eating water birds and marine mammals, may be of concern due to the great biomagnification potential (Senthilkumarl *et al* 2001) associated with trophic level and risk assessment (Zhang *et al* 2011). This study was undertaken within the framework of the French National Research Agency (ANR) program MARSECO. We have chosen PCBs along with OCs pesticides in this work since these two families of persistent organic pollutants (POPs) have several similarities in terms of physco-chemical properties such as semi-volatile, lipophilic, toxic and persistent in the environment. Additionally, both have health effects to human being such as increasing the risk of cancers, have reproductive and developmental effects, cause immunosuppression, decrease IQ, and cause endocrine dysfunction (Hardell *et al* 2010). We investigated the extent of OCs and PCBs in the sediments and their potential recent contamination through indices of pollution and potential environmental risk as well as their temporal trends after the 1970–1980 ban in comparison with other studies in the area.

4.2. Materials and methods

Chemicals

Organochlorine pesticides (OCs) and some related metabolites, such as aldrin, α-, β-, δ-, γ-HCH, dieldrin, α-endosulfan, β-endosulfan, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, methoxychlor, p,p'- dichlorodiphenyldichloroethane (p,p'-DDD), p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), were purchased from Supelco at 2.000 μg ml^{-1} in toluene:hexane (50:50/v:v). PCBs (congeners 28, 52, 101, 118, 138, 153, 180) were purchased in the form of 10 ng.μg^{-1} in iso-octane solution from Dr. Ehrenstorfer (Augsburg, Germany). Mirex PESTANAL was purchased from Sigma-Aldrich (St.

Louis, MO, USA). IUPAC nomenclature of mentioned compounds is in Electronic Supplementary Material (Text 1). Standard working solutions were diluted with dichloromethane (DCM) (SGS, France). Analytical grade solvents used such as acetone (ACE) and n-hexane (HEX) were also purchased from VWR International (Fontenay sous bois, France), Fontainebleau sand was provided by Carlo Erba reagents (Milan, Italy). Alumina, Silica-gel 60 (200–300 mesh) and anhydrous sodium sulfate (Na_2SO_4) were purchased from VWR International. Certified reference material (CRM HS-5) of marine sediment was purchased from National Research Council (Canada).

Sample collection

As shown in Fig. 4.1, samples from 12 stations (three independent subsamples per station) were collected from sewage outfall of the wastewater treatment plant of Cortiou-Marseille, France. Surface sediment samples were collected on 21st March and 23rd June (2010) with a sediment grab sampler (Shiptex; Wildco, USA) and PVC core samplers (ϕ 100 mm) using scuba equipment. The sampling points lie perpendicularly to the coastline (237°N) starting from the sewer outlet to the seaward. All sediment samples were freeze-dried, then sieved using a 2 mm mesh, homogenized and stored at −18°C prior to analysis.

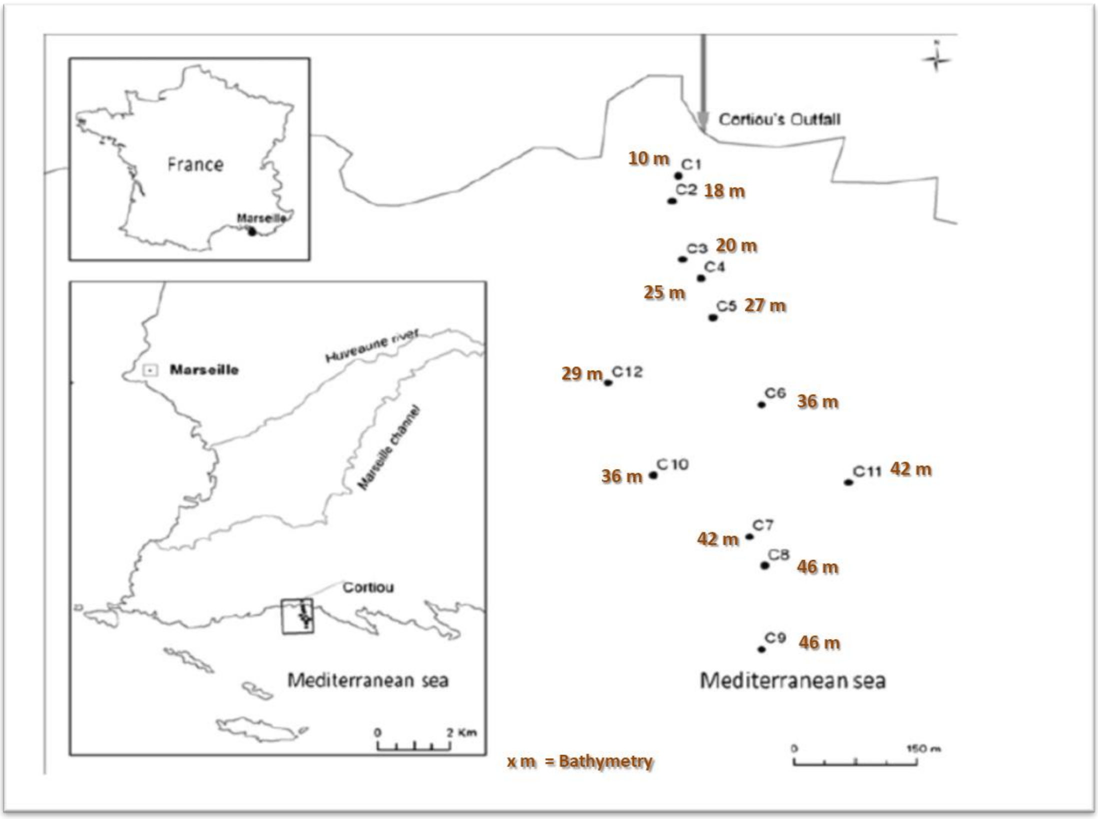


Figure 4.1. Site location and sampling station

Sample extraction and analysis

Sediments (10 g) were thoroughly mixed with anhydrous Na_2SO_4 and 2.5 g of activated copper powder (removal of elemental sulfur). Sediments were then spiked with 1 $ng.g^{-1}$ dry weight (dw) surrogate solution (endrin ketone and PCB 204) and extracted with a 'Soxtherm' device (C. Gerhardt KG, Germany). The program steps were extraction by immersion of the sample in hot solvent

(HEX:ACE, 50:50) at 120°C during 65 min and then under reflux of distillated solvent for 90 min. The extracts were then fractionated and eluted according to Dierking *et al* (2009). Quantitative analyses of OCs and PCBs were carried out using a gas chromatograph (GC) equipped with a GC auto-sampler, split/splitless injector and coupled with a mass spectrometer (Perkin-Elmer Autosystem XL, California, USA). The separation was achieved with a fused silica capillary column (Elite-5MS, 30 m×0.25 mm ID with 0.25-µm thickness film Perkin-Elmer, California, USA). Helium was used as carrier gas at a constant rate of 1 ml.min^{-1}. The temperature program during the run was as follows: initial temperature 50°C, then increased to 100°C at 30°C.min^{-1} and increased to 290°C at 3°C.min^{-1}, held for 5 min. The injector was set at 250°C, and the MS source at 300°C. MS was operated in positive electron ionization (EI) mode (70 eV) using SciFi mass spectra acquisition corresponding to simultaneous full scan (FS) and selected ion resolution (SIR) mode. OCs and PCBs were determined using mirex as internal standard.

Quality control and quality assurance

All data were subject to quality assurance and control procedures. All concentration data are based on dw. The detection limit of organochlorine compounds ranges from 20 to 26 pg.g^{-1} and more specifically 10–30 pg.g^{-1} for DDT class compounds, 5 – 20 pg.g^{-1} for HCH class compounds, and 5 – 26 pg.g^{-1} for PCB congeners. Endrin ketone and PCB 204 were used to measure the recoveries for OCs and PCBs, respectively. The spike recoveries for OCs and PCBs in CRM marine sediment (HS-5) ranged from 85% to 99% and from 94% to 101%, respectively.

4.3. Results and discussion

4.3.1. Organochlorins pesticides

With the exception of a slight coelution between dieldrin and endrin, all OCs and PCB congeners were well resolved and eluted within a reasonable time under the optimized GC conditions. The concentrations of OCs and PCBs are shown in Table 4.1. ΣOCs in these sediments ranged from 1.2 to 190.6 ng.g^{-1} dw of sediment. The highest value was found at the station C1 with a decreasing trend of total OCs concentration seaward. Among these compounds, the concentrations of ΣDDT were the highest, ranging from 0.7 to 114.3 ng.g^{-1} with arithmetic means of 42.7 ng.g^{-1}, followed by those of dieldrin 15.6 ng.g^{-1} (0 to 41.3 ng.g^{-1}), endosulfan sulfate 14.3 ng g^{-1} (0 to 45.3 ng.g^{-1}), ΣHCH averaged 7 ng.g^{-1} (0.1 to 31.4 ng g^{-1}), and β-endosulfan 5.6 ng.g^{-1} (0–11.7 ng.g^{-1}). Other OCs, such as heptachlor, α-endosulfan, endrin, endrin aldehyde and methoxychlor, were present in average concentrations of less than 3 ng.g^{-1}. Heptachlor epoxide was only detected in C2 and C5. Concerning DDT compounds, technical DDT usually contains 75% p,p'-DDT, 15% o,p'-DDT, 5% p,p'-DDE and <5% p,p'-DDD. The average composition of p,p'-DDT congener detected in the sediment samples was 28% (2.4%–54.1%), p,p' DDE 16.4% (0.5%–30.5%), and p,p'-DDD 53.8% (2.45%–96.1%). Figure 2 presents the relative amounts of different metabolic forms of DDT detected at the different stations. The grey zone can be considered as a benchmark of technical DDT. Considering no recent input and the fact that sediment samples are presumably anaerobic, the increase of DDD metabolites probably results from biodegradation processes linked to anaerobic reductive dechlorination. As shown in Fig. 2, stations C1– C4 and C11 might be attributed to anaerobic transformation of DDT while C10 refers to the aerobic one. Moreover, C5, C6, C8, C9 and C12 reflect mixed mode of DDT metabolites transformations, while C7 corresponds to a recent input or an absence of biodegradation. Lee *et al* (2001) proposed the use of the ratio p,p'-DDT/ΣDDT>0.55 to indicate a recent input of technical DDT due to high concentration of p,p'-DDT found in the sediment compared with its metabolites. Our results show a ratio ranging from 0 to 0.7 with an average of 0.3. With the exception of C7, which has a ratio of 0.7, most of the sediments indicate that technical DDT input was historical. Additionally, a ratio of (DDE+DDD)/ΣDDT>0.5 may indicate a selective degradation of DDT (Hites and Day 1992). The calculated ratio of (DDE+DDD)/ΣDDT in Cortiou sediments ranged from 0.3 to 1.0 (arithmetic mean 0.7), reflecting that such degradation had occurred. Recent work suggests that this index value is the result of long-term weathering (Zhao *et al* 2010). Compared with two previous studies at the same site, we observed a marked decrease over the time of ΣDDT from 2–1,585 ng.g^{-1} in Arnoux *et al* (1980) to 2–250 ng.g^{-1} in Wafo *et al* (2006). Since the sewage outfall from WWTP of Marseille constitutes the main input (Arnoux *et al* 1980) and DDT half-life in soil and sediments have been estimated in the range of 6–30 years (Hites and Day 1992), our results suggest that no recent important DDT input has occurred since these decreasing trends were elucidated. Concerning endosulfan congeners, we found α-endosulfan, β-endosulfan with respective average concentrations of 2.5 ng.g^{-1} (ranged from 0 to 6.5 ng.g^{-1}) and 5.6 ng.g^{-1} (nd to 10.7 ng.g^{-1}). Typical technical mixtures contain approximately 70% α-endosulfan and 30% β-endosulfan. Figure 4.3 represents a metabolic forms chart of endosulfan in the sediment with the estimated binary technical formulation located in the grey zone. α-Endosulfan is known to be thermodynamically more stable than β-endosulfan (Schmidt *et al* 2001). In addition, abiotic processes can slowly but irreversibly convert β-endosulfan to α-endosulfan (Schmidt *et al* 2001). Surprisingly, our results showed a systematic transformation of α-endosulfan as most stations exhibit less than 30% of α-isomer. Interestingly, it coincides with the highest concentration of endosulfan sulfate among endosulfan congeners, suggesting a transformation process through oxidation or indirectly via slow hydrolysis forming diol to breakdown endosulfan (Shivaramaiah and Kenedy 2006). Figure 3 shows that endosulfan metabolic forms are dominated by more than 50% of endosulfan sulfate. Meanwhile, according to EPA (2002), and due to the structural similarity with the parent compound and persistency, the presence of endosulfan sulfate is also subject to toxicological concern. The half-life of endosulfan isomers and metabolites range from 9 months to 6 years (EPA 2002). Assuming that in Marseille, after the European Union’s 2007 ban, there has been no further release into the environment, it will be a decade before these toxic residues disappear.

Table 4.1. Concentration (ng.g^{-1}) of organochlorines pesticide in superficial sediment samples collected from Cortiou sampling stations (C1–C12).

Cortiou's station	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**
p.p' DDE	0.4	2.8	1.2	3.2	4.8	2.8	3.3	0.3	0.7	1.1	0.1	0.2
p.p'DDD	85.5	93.8	76.7	90.1	23.6	3.6	4.6	2.4	1.5	0.1	0.9	0.2
p.p'DDT	3.1	17.6	1.9	14.2	28.7	5.4	20.7	3.1	1.4	0.1	0.2	0.2
α Endosulfan	3.7	0	2	2.2	6.5	4.3	3.3	0.3	0.4	1.9	0.6	0
β Endosulfan	10.7	5.2	10.5	2.3	11.7	10	6.8	0.5	0.5	2.4	1.2	0
Endosulfan sulfate	28.1	8	2.4	24.8	45.3	15	25.1	6.8	0.3	0	1.4	0.4
α-HCH	1.5	1.8	0.9	3.4	3.8	2.3	1.3	0	0	0	0	0.1
β-HCH	2.6	2.4	2.5	1.2	1.2	7.5	1.6	0	0.1	0.1	0.1	0
γ-HCH	0.6	1.7	2.3	0.4	2.6	3.9	1.2	0	0	0.2	0	0
σ-HCH	9.6	0.9	0.4	1.4	3.7	17.7	0.8	0.1	0	1.6	0.2	0
Endrin	1.4	1.5	0	4.5	5.4	2.2	3.5	0.7	0.3	0.6	0.3	0
Endrin aldehyde	0.2	0.3	0.4	0.3	0	0	0.1	0	0	0	0	0
Endrin ketone	0.3	0	1.5	0.5	3.2	0.3	2.4	0.2	0.4	0.4	0.1	0
Dieldrin	41.3	21.2	17	20.2	30.7	21.2	12.1	2	3.3	1.4	1.2	0
Aldrin	0.3	0.5	1.1	0.9	2.6	0.7	0.8	0.1	0	0.1	0.1	0
Heptachlor	0.7	0.4	0	0.7	0	0.4	0.1	0	0	0.1	0	0
Heptachlor epoxyde	0	1.5	0	0	0.2	0	0.1	0	0	0	0	0
Methoxychlor	0.6	3.9	3	2.5	8.1	4.8	6.2	0.8	0.8	1.2	0.3	0
ΣHCH	14.3	6.7	6.1	6.4	11.4	31.4	5	0.1	0.1	2	0.3	0.1
ΣEndosulfan	42.5	13.2	14.9	29.3	63.5	29.4	35.2	7.6	1.2	4.3	3.2	0.4
ΣDDT	89	114.3	79.8	107.5	57.1	11.7	28.6	5.8	3.6	1.3	1.2	0.7
ΣOCs	190.6	163.7	123.7	172.6	182.2	102	93.9	17.2	9.6	11.5	6.7	1.2

According to the literature, HCH consists of eight isomers (Safe 1993) although commercially a technical grade of HCH is a mixture of mainly four isomers, α-HCH (60%–70%), β-HCH (5%–12%), γ-HCH (10%–15%) and δ-HCH (6%–10%) (Kutz *et al* 1991). At the stations where the whole isomers were found (C1–C7), the average composition of HCH isomers are 24.5% α-HCH (7.3 – 52.7%), 25.8% β-HCH (10.4% – 40.4%), 19.9% γ-HCH (3.9% – 37.8%), and 30.5% δ-HCH (6.2% – 67%). On average, the concentrations of δ–HCH were highest among the HCH isomers followed by β–HCH, α-HCH and γ-HCH (Table 4.1) with respective values of 3.6, 1.9, 1.8 and 1.6 ng g^{-1}, respectively. Concerning δ-HCH, we suggest that the highest values of K_{ow} and K_{oc} compared to other isomers contribute to their persistence in sediments by undergoing adsorption/desorption phenomena. Regarding their physical–chemical properties, α-HCH and γ-HCH are known for their high Henry's constant value (6.86×10^{-6} and 3.5×10^{-6}, respectively) leading to a better intercompartment mobility for α- and γ-isomers compared to δ-HCH and β-HCH (2.1 and 4.5×10^{-7}, respectively; HSBD 2003). On the other hand, β- and δ-HCH isomers have the lowest water solubility and vapor pressure (HSBD 2003), hence a better stability toward physicochemical parameters including microbial attack (Lee *et al* 2001). As can be seen in Fig. 4.4, technical HCH formulation contains 60%–70% of α+γ-HCH.

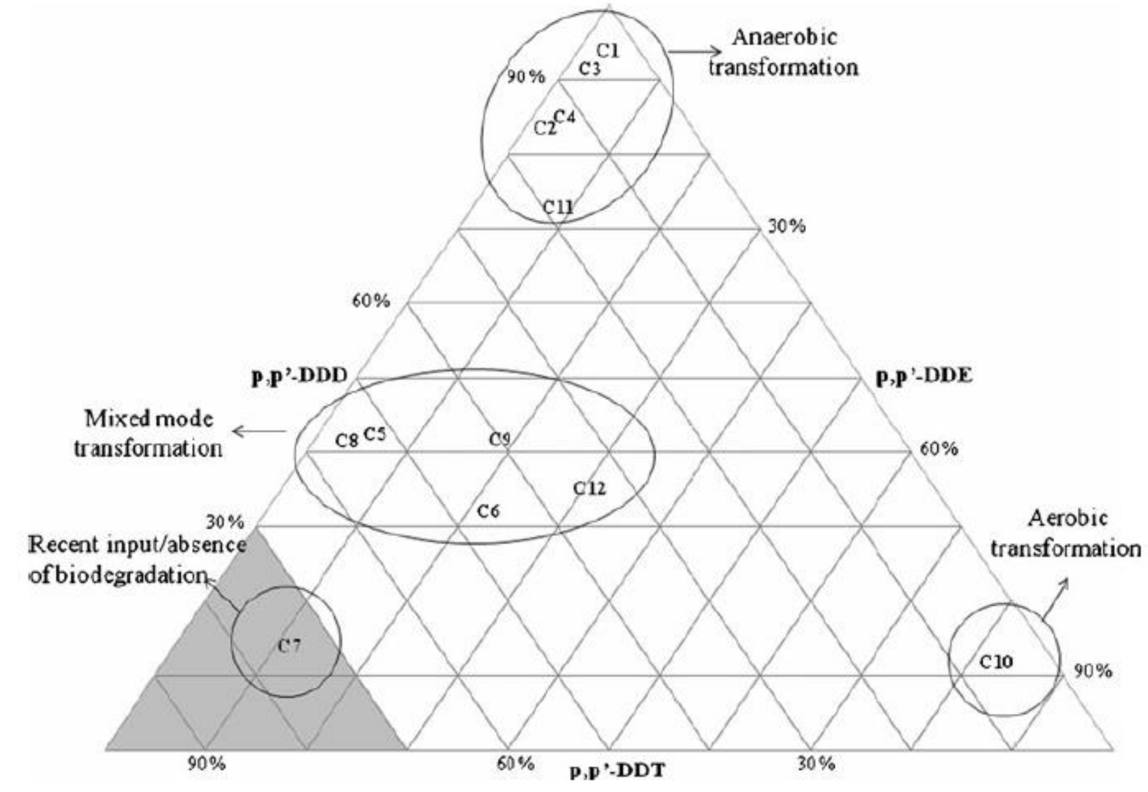


Figure 4.2. Ternary diagram showing the relative amounts of different metabolic forms of DDT in Cortiou sediment. The grey zone can be considered as a benchmark of technical DDT containing 75% p,p'-DDT, 5% p,p'-DDE, and <5% p,p'-DDD.

Thus, our results show a continuum of degradation from C2, C3, C4, C5, C7 which are close to a technical mixture, while C1, C6, C8, C9, C10 and C11 show significant depletion of α- and γ-HCH isomers, probably due to long-term weathering. However, the isomer balance for C12 might be an indication of a selective degradation but this result should be confirmed. Endrin is an organochlorine alicyclic insecticide that also exists as a byproduct in aldehyde and ketone forms and is closely related to dieldrin and aldrin. Endrin was detected in Cortiou's sediments with a concentration range of 0 to 5.4 ng.g^{-1} (average 2 ng.g^{-1}). Such compounds may be broken down through biodegradation processes, high temperatures or light to form endrin ketone and endrin aldehyde (Wang *et al* 2006). Endrin was banned in France in 1994. Nevertheless, Fig. 4.5 demonstrates either potential recent use of endrin formulation or compound persistency because most of the stations were found at the maximum range of the endrin sphere. Hence, the presence of endrin ketone and endrin aldehyde in these sediments may be a proxy of transformation processes that have taken place in the past. Due to its chemical stability and lipophilicity, dieldrin is extremely persistent in sediments. This study has shown that, despite agricultural restrictions from the early 1980s onwards, dieldrin was detected in Cortiou sediments with a concentration between 0 and 41.3 ng.g^{-1} (the average was 15.6 ng.g^{-1}). Villeneuve *et al* (1999) found that dieldrin concentration ranged from 27 to 36 ng.g^{-1} in Cortiou's sediments. Such decrease can be attributed to the degradation/mineralization of dieldrin in the sediments (Chiu *et al* 2005 ; Maule *et al* 1987). Moreover, for the urban area of Marseille, we have to consider that other activities, such as the textile industry, use formulations containing dieldrin (Shaw 1994) for wool storage and transportation. This can potentially contribute to the dieldrin persistency in Cortiou's sediments. Concerning aldrin, this study has shown concentrations ranging from 0 to 2.6 ng.g^{-1}. It is well known in the environment that aldrin is readily converted to dieldrin. Assuming that both aldrin and dieldrin were largely used before, dieldrin seems to be more resistant to biodegradation than aldrin which has been found only in low concentration (Table 4.1). For other OCs pesticides, the study revealed concentration of heptachlor and heptachlor epoxide ranging from nd to 0.7 ng.g^{-1} and from nd to roughly 1.5 ng.g^{-1}, respectively. Again, even though their use has been banned since 1988, their highly stable structure means that heptachlor and heptachlor epoxide can persist in the environment for decades. For instance, heptachlor halflife has been reported to be 16 years in soil (Olafdottir *et al* 2005). Technical grade heptachlor usually consists of 72% heptachlor and 28% impurities such as transchlordane, cis-chlordane and nonachlor (HSDB 2007). Heptachlor can be biotransformed by microorganisms and animals through epoxidation (heptachlor epoxide), hydrolysis and reduction. Indeed, at several stations (C2, C5 and C7), we found that the extent of heptachlor epoxide implies the occurrence of effective biodegradation of heptachlor in the sediments. However, we have to take into consideration the fact that metabolized heptachlor is potentially more toxic than its parent compound. In aquatic systems, heptachlor epoxide has been reported to have bioconcentration factors of 200 – 37000 for some aquatic species. Nowadays, heptachlor can only be used for ant control in underground power transformers (Agency for Toxic Substances and Disease Registry (ATSDR 2007).

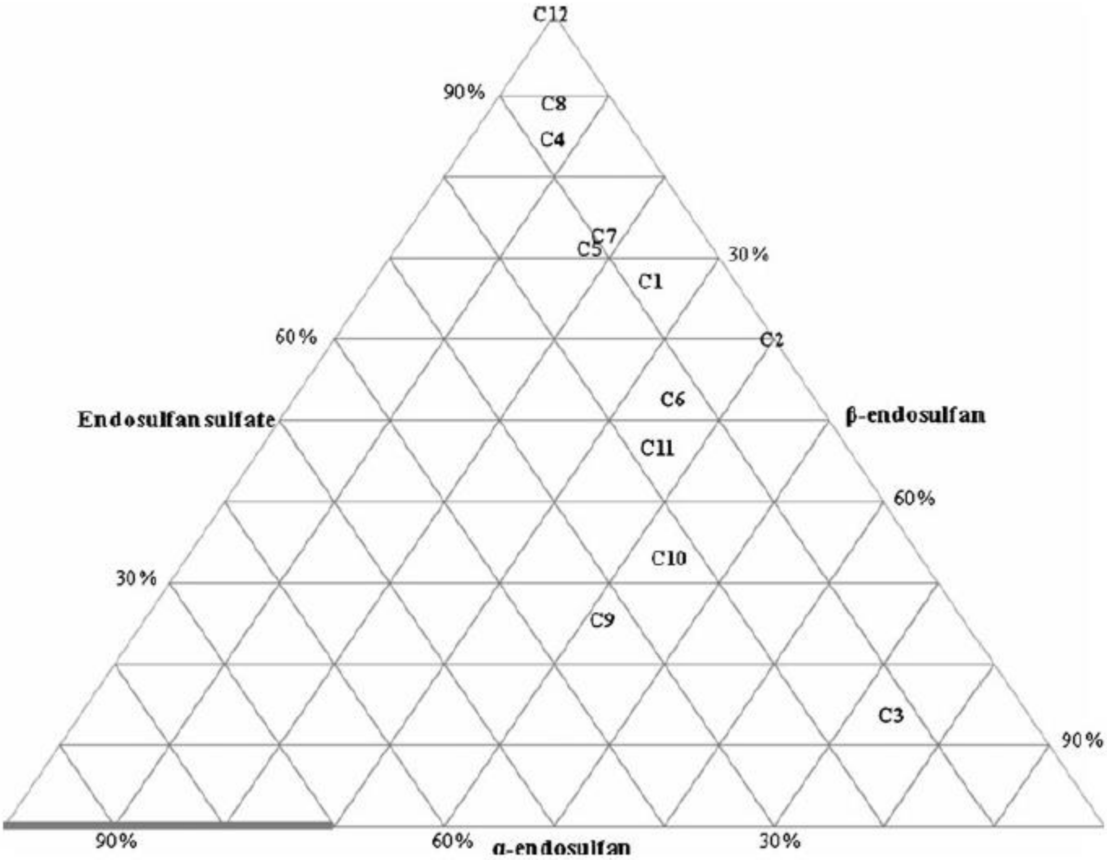


Figure 4.3. Ternary diagram showing the modification of relative amounts of α- and β-endosulfane including endosulfane sulfate as their transformation product in Cortiou sediment. The grey zone can be considered as a benchmark of technical endosulfane compound containing 70% α-endosulfane and 30% β-endosulfane.

To our knowledge, this is the first time that methoxychlor has been detected in Cortiou sediments. Indeed, little information is available regarding the environmental transport and partitioning of methoxychlor in the marine environment including acute toxicity for the living biota. Methoxychlor has potentially endocrine-disrupting properties and it was included in the OSPAR List of Chemicals for Priority Action in 2000 (OSPAR Commission 2002). You *et al* (2004) determined the 10-day sediment LC_{50} values for methoxychlor as 36.7 and 85.8 $ng.g^{-1}$ using the aquatic invertebrates Hyalella azteca and Chironomus tentans. Our results show that concentrations varied from nd to 8.1 $ng.g^{-1}$, which is far below the abovementioned value. Although methoxychlor is predominantly biodegraded in sediments under anaerobic conditions, its consumption has risen because it is used as an insecticide for home and garden application as it has less residual effect compared to DDT (Muir and Yarechewski 1984). Additionally, this compound might be a potential marker of the impact of urban activities in the marine environment. To conclude, although some effort has been made to reduce contamination through WWTP, the contamination of the OCs in Cortiou sediments occurred and could still have an adverse effect on the environment.

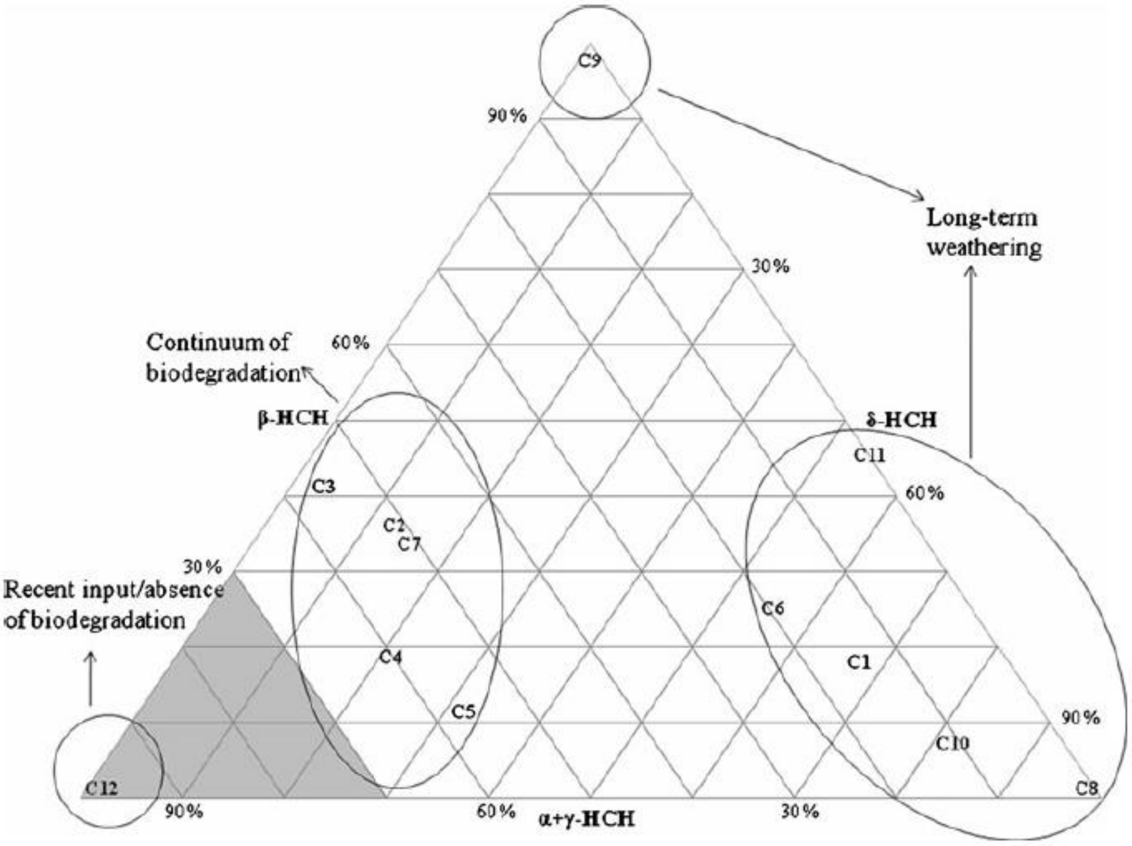


Figure 4.4. Ternary diagram showing the relative amounts of different metabolic forms of HCH in Cortiou sediment. The grey zone can be considered as a benchmark of technical HCH containing 60%–70% α-HCH, 5%–12% β-HCH, 10%–15% γ-HCH and 6%–10% δ-HCH

4.3.2. Polychorinated biphenyls

Coplanar indicator PCB congeners CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180 were detected in all sediment samples. Table 4.2 shows that the total PCB concentrations ranged by more than two orders of magnitude from 9.1 to 226.9 ng.g^{-1} with an average value of 84.3 ng.g^{-1}. Individually, the dominant coplanar congeners (>50 ng.g^{-1}, on average) were CB-153, CB-138 and CB-101. The horizontal distribution of total PCBs in Cortiou surface sediments revealed that concentrations varied widely, depending on the stations. Generally, PCBs concentrations at stations C2, C3, C5 and C7 were highest, while stations C10, C11 and C12 were lowest, demonstrating that concentration roughly decreased with distance from Cortiou's outfall. Surprisingly, at station C1, total PCBs did not exceed 10 ng.g^{-1}. An explanation for this is that interstation variability may be due to the complex hydrodynamic conditions taking place in front of Cortiou's outfall (4 M^3. s^{-1}). Several authors state that hydrodynamic conditions are the most important influencing factors effecting the distribution of PCBs in surface sediments (Zhang *et al* 2007; Tang *et al* 2000). Such a trend has previously been observed by Wafo *et al* (2000).

Table 4.2. Concentration (ng.g^{-1}) of PCBs in superficial sediment samples collected from Cortiou sampling stations (C1–C12) Cortiou's station.

Cortiou's station	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**
CB-28	0	19.8	33.2	45.2	29.5	10.9	15.1	26.8	13.9	0	1.3	1.5
CB-52	4.1	33.9	33.8	34.4	15.8	3.4	44.6	13.8	7.3	0.1	0.8	0.9
CB-101	6.3	124.4	103.5	124.2	35.7	15.5	165	60.5	20.9	0.9	3.8	4
CB-118	5.3	110.2	85.5	92.2	26.1	10.1	162.4	39,.6	16.7	1	3.4	3.5
CB-138	10.9	171.1	106.3	132.3	37.1	20.1	171.6	81.5	36.9	2.9	0.7	0.8
CB-153	4.7	174.4	109.5	131.4	60.4	32.6	152.2	96.2	33.2	5.1	7.3	7.8
CB-180	1.2	97.7	39.7	59.9	6.9	3.2	80.7	20.6	10.6	1.5	1.6	1
Σ7PCBs(ICES)	32.5	731.5	511.5	619.7	211.4	95.8	791.5	339	139.6	11.5	18.8	19.4
DP-6Eq[a]	77.5	1349.7	831.6	1014.2	318.1	160.9	1382.7	580.4	237.7	25.8	31.6	31.8
Arochlor 1260eq[b]	142.8	2479.6	1733.8	2100.6	716.5	324.9	2683.1	1149	473.1	39.1	63.8	65.7

CB Chlorobiphenyl, ICES International Council for Exploration of the Sea, eq equivalent

[a] Expressed as (CB-118+CB-138+CB-153+CB-180) × (100/41) (Wafo *et al* 2006)

[b] According to Frame *et al* (1996) and Gomez-Gutiérrez *et al* (2007)

Concerning PCBs congeners, those containing 3 – 5 Cl atoms were reported to be major components (>90%) of commercial mixtures released into the environment (Zhang *et al* 2007). Relative environmental homolog contribution reported by some authors showed decreasing abundance as a function of the number of chlorine atoms, i.e., 3> 4> 5> 2> 6 >7 (Zhao *et al* 2010.) Alvarez Piñeiro *et al* (1996) suggested that the higher chlorinated compounds are less mobile, hence closer to the contamination source, in comparison to less chlorinated derivatives. Our results are in good agreement as we found important removal of PCB congeners containing 3 – 4 chlorine atoms to the detriment of 5 – 7 Cl congeners. Indeed, highly chlorinated PCBs have a high K_{ow} value, meaning that they are easily adsorbed by suspended particulate matters and are not easily biodegraded.

Table 4.3. Comparison of PCB concentrations in the surface sediments of Cortiou and other coastal areas worldwide (ng.g^{-1})

Sites	**Country**	**PCBs extent (ng.g^{-1} dw)**	**References**
Mediterranean basin			
Cortiou Outfall	France	11.5 - 751.5	This study
		15 - 15.800	Arnoux *et al* 1980
		3350 - 14773	Bellemin-Guyot 1982
		5503 - 22900	Lecouffe 1986
		23 - 700	Monod *et al* 1987
		461 - 1559	Wafo *et al* 2006a
Seine River		50 - 26000	Chevreuil *et al* 1988
Thau Lagoon		0 - 28.3	Leaute 2008
Venice Lagoon	Italy	6 - 1590	Frignani *et al* 2001
Mark Piccolo, Taranto		2 - 1684	Cardelicchio *et al* 2007
Ebro River	Spain	5.3 - 1772	Fernandez *et al* 1999
Manzala Lake	Egypt	125 - 330	Yamashita *et al* 2000
Nile River		1.5 - 2.2	El-Kady *et al* 2007
Alexandria Harbor		0.9 - 1211	Barakat *et al* 2002
Other Basins			
Istambul Strait	Turky	0.02 - 540	Okay *et al* 2009
Scheldt River	Bbelgium	105 - 400	Covaci *et al* 2005

Mersey Estuary	UK	39 - 1409	Vane *et al* 2007
Ontario Lake	Canada	2.6 - 255	Marvin *et al* 2004
Hudson River, New York	USA	80 - 1410	Feng *et al* 1997
Yellow River	China	1.4 - 5.3	He *et al* 2006
River in Tianjin		44 - 154	Liu *et al* 2007

CB Chlorobiphenyl Expressed as (CB-118+CB-138+CB-153+CB-180) × (100/41) (Wafo *et al* 2006)

The source of these congeners may be due to historical discharge with high concentrations of PCBs (Arnoux *et al* 1980; Bellemin-Guyot 1982; Lecouffle 1986) and the fact that these compounds are extremely persistent. Unintentional release of PCBs from Marseille's industrial and urban areas may be another explanation for the extent of the PCBs in sediments. Thus, PCBs may bind to particulate and suspended matter before accumulating in the sediment, after they have passed through Cortiou's outfall. The predominance of such environmentally persistent compounds has been reported in various environmental matrices emitted from industrial and urban areas (Gatehouse 2004). Indeed, through sea current and atmospheric deposition, influence from the industrial activities of the Gulf of Fos (iron and steel industries, chemistry, incineration of industrial waste, oil refineries) can also be the source of such pollutants.

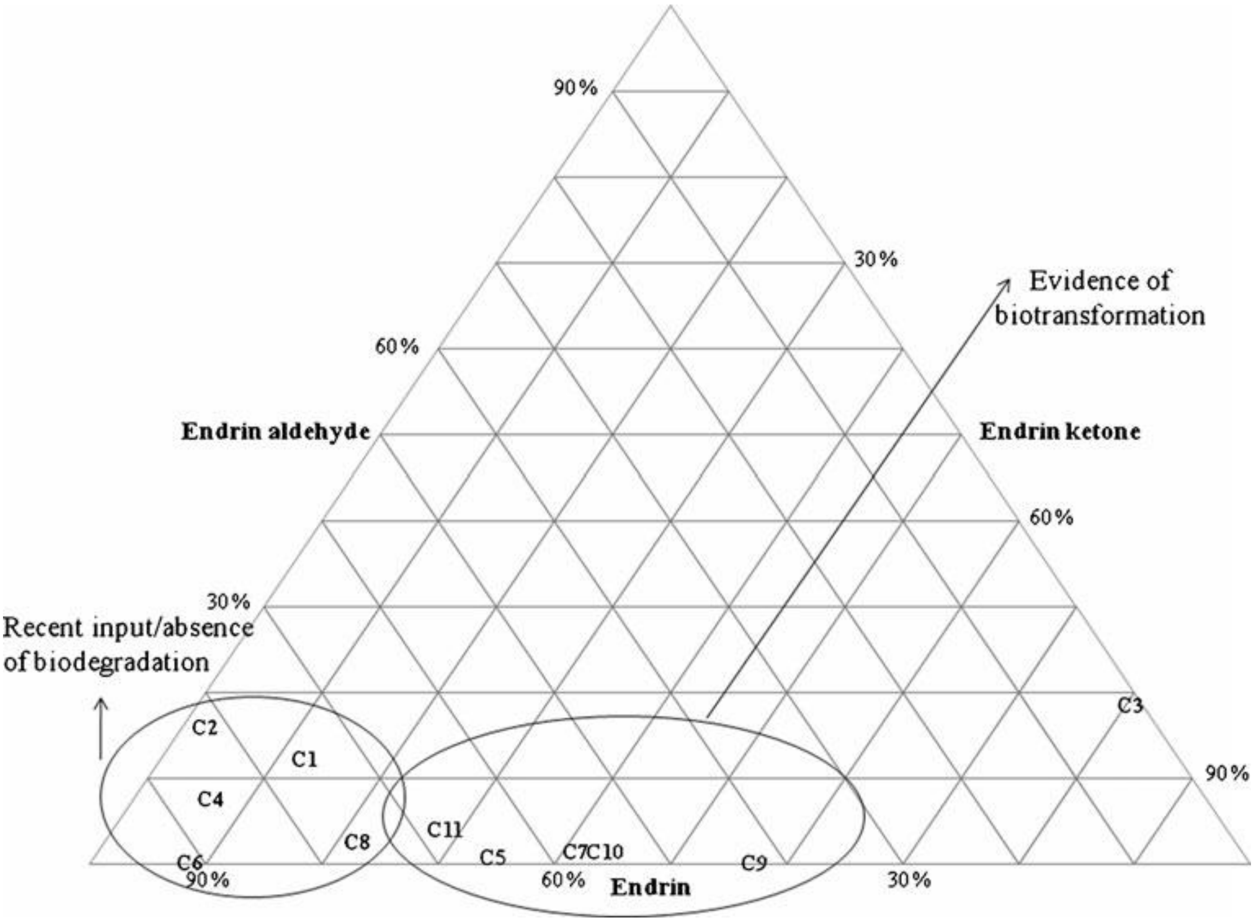


Figure 4.5. Ternary diagram showing the occurrence of relative amounts of endrin, endrin aldehyde, and endrin ketone in Cortiou sediment.

Other potential urban/industrial PCB contaminants include transformers, capacitors, ink, paper, paints, fire retardants and lubricants. (Tolosa *et al* 1997) have estimated that sewage outfalls may contribute less than 10% of PCBs into the NW Mediterranean, whereas rivers and atmospheric deposition are the principal contributors, particularly, in the west area of Cortiou (Dierking *et al* 2009). In order to compare the levels of selected PCBs in harmonized data, we used seven individual congeners (CB-28, CB-52, CB-101, CB-118, CB-153, CB-138 and CB-180) which were recommended by the International Council for the Exploration of the Sea (Duinker *et al* 1988; ICES), although some authors also referred to commercial formulations, such as Aroclor 1260, DP-5 and DP-6 (Phenochlor), or mixtures of them (Gomez-Gutiérrez *et al* 2007 ; Wafo *et al* 2006). According to this, for example, the seven PCB congeners recommended by the ICES represent 29.5% w/w of Aroclor 1260 mixture (Gomez-Gutiérrez *et al* 2007). Concerning DP-6, (Wafo *et al* 2006) mentioned that this mixture is an industrial component widely used in France, representing 41% of the total amount of used PCBs. In the study area, our results confirm the persistency of PCBs over the time (Tables 4.2 and 4.3). Marseille's WWTP chemical assisted sedimentation (primary treatment) was deployed in 1987, while secondary treatment process (biological) started only in 2007. Compared to recent work in the area (Wafo *et al* 2006), which can be considered as a reference for the effectiveness of the secondary treatment (2007), we found a slight decrease in total PCB (expressed in DP-6 ; Table 4.2) at most stations (C1, C5, C6, C9, C10, C11 and C12). It is nevertheless delicate to link such a decrease to merely degradation processes, as simple dilution phenomena may take place due to the huge release of suspended matters from the Cortiou outfall. Furthermore, unequivocal biodegradationcould be evidenced with extensive congener analyses (selective degradation) and a long-term monitoring program.

Data comparison of PCBs concentration in the sediments from different ecosystem type and region is not always easy due to the different modes of expression and individual congeners found. For instance, Gomez-Gutiérrez *et al* 2007, reported PCBs levels in sediments of 1 – 16.916 ng.g^{-1} for harbours, 0.9 – 5,600 ng.g^{-1} for coastal lagoons, 0.4–15,815 ng.g^{-1} for urban-influenced regions, 0.5 – 1,500 ng.g^{-1} for river-influenced regions, 0.05 – 1,200 ng.g^{-1} for the continental shelf and 0.3–48 for open sea (depth>1,000 m). PCBs concentrations in surface sediments of Cortiou were in the same orders of magnitude compared to most of the coastal/riverine/estuaries systems in the Mediterranean basin. However, the concentration of total PCBs in the Cortiou area are one to three orders of magnitude higher than Ontario lake in Canada and two rivers in China (Electronic Supplementary Material, Table 4.3).

4.3.3. Principal component analysis

A statistical approach using principal component analysis (PCA) was performed on the average concentration of OCs and PCBs from the 12 stations. The first two principal components displayed by PCA explained 70.4% of the total variance (40% PC1 and 30.4% PC2) and discriminate between two groups of stations (C2–C7) and (C1, C8–C12; Electronic Supplementary Material, Fig. 4.6). The first group (C2–C7) showed a negative correlation with PC1 revealing that the concentration of pollutants varied as a function of outfall distance, salinity decrease and depth. The most representative compounds explaining PC1 were p,p'-DDT, heptachlor and p,p'-DDE. The positive part of PC2 was associated with the high levels of Σ7PCBs (ICES) in C2, C4 and C7, while endrin aldehyde, heptachlor epoxide and p,p-DDD were particularly represented at station C3. β-HCH, δ-HCH and α-endosulfan were associated to the negative part of PC2 with high concentrations at C5 and C6. The remaining OCs (α-HCH, γ-HCH, endosulfan sulfate, β-endosulfan, dieldrin, endrin, endrin ketone and metoxychlor) contribute to the negative parts of both PC1 and PC2. Furthermore, half of the data are distributed along the positive axis of PC2, which explains 30.4% of the variance. We suggest that physicochemical properties of contaminants may also play a role in their distribution, as they were separated along the positive axis of PC2, which is characterized by PCBs congeners, while most of the OCs contributed to the negative axis of PC2.

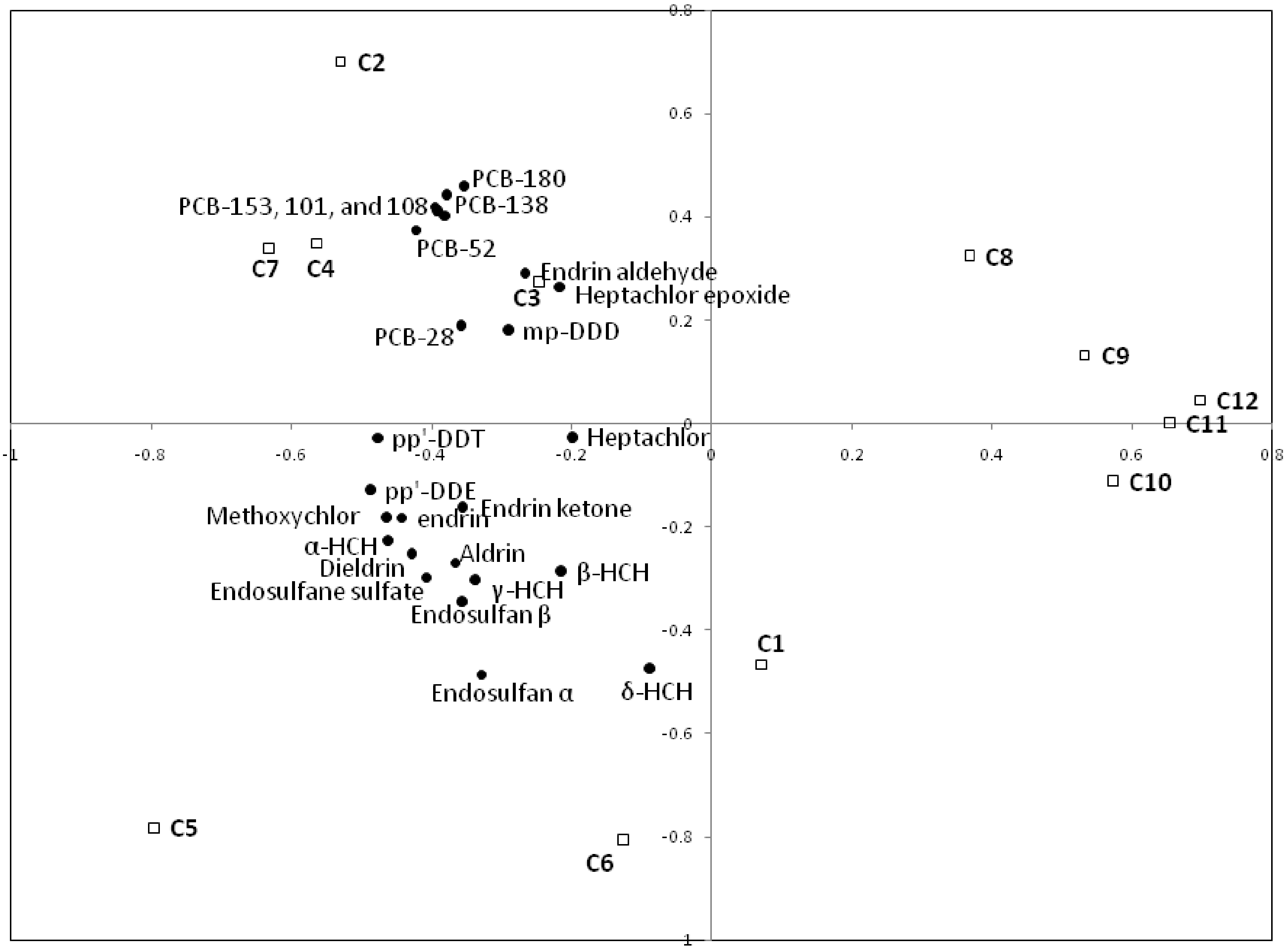


Figure 4.6. Principal component analysis (PCA) loading plots for sediment samples collected from Cortiou sampling stations (C1 – C12) for organochlorine pesticides and polychloro-Biphenyls compound distribution.

4.3.4. Environmental significance

To evaluate the environmental significance of OCs and PCBs occurrence, we compared our data with consensusbased marine sediment quality guidelines (SQGs; Gomez-Gutiérrez *et al* 2007 and references herein) using threshold effect concentration (TEC) and probable effect concentration (PEC). The SQGs index was already available for PCBs, but for OCs, the values were only available for total DDT, calculated following the methodology described by MacDonald *et al* (2000). TEC and PEC values for DDTs were 2.5 and 39 ng.g^{-1}dw compared to 29 and 274 ng.g^{-1} dw for PCBs, respectively. Our study showed that total DDT varied from 57.1 to 114.4 ng g^{-1} dw (C1 – C5), from 3.6 to 28.6 ng g^{-1} dw (C6 – C9) and from 0.7 to 1.3 ng.g^{-1} of dw (C10 – C12). In terms of ecological risk, the results indicate a potential adverse effect on marine biota (>39 ng g^{-1} dw), particularly at stations less than 0.5 km from sewer outfall (C1 – C5). Sampling points C6–C9 are situated between 0.5 and 1 km from the coast with DDT total extent above the threshold level (TEC; between 2.5 and 39 ng.g^{-1} dw) reflecting a potential toxicity. However, according MacDonald *et al* (2000), adverse effects are uncertain yet. No ecological risk appears to exist at stations C10–C12. In the same way, we observed an excessive value of PCBs content in the sediments when compared to TEC, with the exception of C10–C12. In general, when the concentrations are between TEC and PEC values, it indicates that sediments have a potential toxicity with probable adverse effects (C1, C5, C6 and C9). Higher levels of PCBs, above PEC values, were found at C2–C4, C7 and C8. These reflect potential toxicity and adverse effect for marine biota and more particularly for benthic communities**.** Risk evaluation of PCBs and OCs has been previously reported by Wang *et al* (2007) in surface sediment samples of three selected rivers in Northeast China using interim sediment quality guidelines (ISQG) and probable effect level (PEL). The ISQG and PEL values reported for total DDT were 3.9 and 51.7, while 34.1 and 277 for total PCBs, respectively. Accordingly, ISQG correspond to threshold level effects below which adverse biological effects are not expected, while PEL defines the level above which adverse effects are expected to occur frequently. Another system, namely, Norwegian environmental quality classification system, for contaminants in seawater and sediment has been published by Bakke *et al* (2010). Referring to these authors, it could be suggested that 50% of Cortiou’s sediment is good (no toxic effects) to moderate (toxic effects following chronic exposure) for total DDT. For total PCBs, sediments could be classified as good (8%), moderate (42%) and bad (50%), reflecting toxic effects following short-term exposure. The environmental significance and toxicological implications of PCBs and OCs indicate that these compounds are bioaccumulative chemicals of concern. These chemicals tend to increase in concentration in the tissue of animals belonging to higher trophic levels, including humans (Safe 1993). Skarphedinsdottir *et al* (2010) elucidated bioaccumulation and biomagnifications of PCBs particularly for penta- or higher chlorinated congeners (e.g., CB-101, CB-118, CB-138, CB-153 and CB-180) and OCs (e.g., total DDT and total HCH) in trophic levels using an isotopic approach (δ15N). Accordingly, in the sediment of Cortiou, it can be speculated that the study area carries an ecological risk.

4.4. Conclusion and perspectives

This study quantifies OC and PCB levels in the sediments directly influenced by the Cortiou outfall of Marseille WWTP. OCs and PCBs levels detected in this area indicate a noticeable decrease compared to previous studies. The POPs extent confirmed successful banning of these compounds throughout Europe in the 1970s. Using selected metabolic compound form tracers of pollution, we have demonstrated the long-term contamination input of OCs (DDT, endosulfan, HCH and heptachlor cases) rather than recent release (dieldrin, aldrin and methoxychlor cases). The best explanation for the detection of OCs and PCBs today is mainly due to their persistence, long half-life and to the lipophilicity of the parent compound as well as of the metabolic forms in which they transform. Even though there is a continuous decrease in these compound concentrations, remaining compounds and their metabolites could have a potential adverse effect for living biota and constitute an environmental risk.With respect to determined PCBs and DDT contaminations, the study area can be qualified as a site of particular concern. Thus, in the perspective of the Calanque National Park, which can be considered as a wise undertaking in the light of the ecological fragility of this area, monitoring and surveillance of xenobiotic remediation should be undertaken as well as the appropriate mitigation measures.

Acknowledgements. The authors acknowledge the financial support of ANR CES grant for MARSECO Project. This work was done in the framework of the research federation ECCOREV. The authors specially thank the PROTEE team from the University of Toulon, Mr. Max Bresson and Mr. Jean François Barbion for their assistance during sampling trips. The authors would also thank Dr. Nick Marriner for rereading the manuscript. We also thank the anonymous reviewers for their constructive comments. ADS gratefully acknowledges De Valroger, F and D. Eric for help with Scuba diving and sediment sampling.

References

Aboucaya A, Verlaque R, Guyot I (2001) La conservation des plantes rares et menacées en France. In Gomez-Campo C (ed) Conservation de especies vegetales amenazadas en la region mediterrànean occidental. R Areces Edit 199–227.

Agency for Toxic Substances and Disease Registry (ATSDR) (2007) Toxicological profile for heptachlor and heptachlor epoxide (update). U.S. Department of Public Health and Human Services, Public Health Service, Atlanta, GA

Alvarez Piñeiro ME, Lage Yusty MA, Simal Lozano J, Gonzalez-Barros CST (1996) PCB and PCT levels in cultivated and free-living mussels of galicia (North west Spain). Toxicol Environ Chem 55:31–36.

Arnoux A, Blanc A, Jorajuria A, Monod JL, Tatossian J (1980) Etat actuel de la pollution sur les fonds du secteur de Cortiou (Marseille). Vème Journées. Etudes Pollutions. C.I.E.S.M, Cagliari, pp 459–470.

Bakke T, Kallqvist T, Ruus A, Breedveld GD, Hylland K (2010) Development of sediment quality criteria in Norway. J Soils Sediment 10:172–178.

Barakat AO, Kim M, Qian Y, Wade TL (2002) Organochlorine pesticides and PCB residues in sediments of Alexandria Harbour, Egypt. Mar Pollut Bull 44:1421–1434.

Bellemin-Guyot C (1982) Bilan de la pollution par les Polychlorobiphényles du milieu Littoral de la région Marseille et des fonds de la Méditerranée occidentale. Thèse de Pharmacie, Aix-Marseille II, pp 1–100.

Cardellicchio N, Buccolieri A, Giandomenico S, Lopez L, Pizzulli F, Spada L (2007) Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian sea, Southerne Italy). Mar Pollut Bull 55:451–458.

Carvalho FP, Villeneuve JP, Cattini C, Rendón J, Mota de Oliveira J (2009) Pesticide and PCB residues in the aquatic ecosystems of Laguna de Terminos, a protected area of the coast of Campeche, Mexico. Chemosphere 74:988–995.

Chevreuil M, Blanchard M, Teil MJ, Chesterikoff A (1998) Polychlorobiphenyl behaviour in the water/sediment system of the Seine River, France. Water Res 32:1204–1212.

Chiu TC, Yen JH, Hsieh YN,Wang YS (2005) Reductive transformation of dieldrin under anaerobic sediment culture. Chemosphere 60:1182–1189.

Covaci A, Gheorghe A, Voorspoels S, Maervoet J (2005) Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt River (Belgium): analytical and depth profiles. Environ Int 31:367–375.

Dierking J, Wafo E, Schembri T, Lagadec V, Nicolas C, Letourneur Y, Harmelin-Vivien M (2009) Spatial patterns in PCBs, pesticides, mercury and cadmium in the common sole in the NW Mediterranean Sea, and a novel use of contaminants as biomarkers. Mar Pollut Bull 58:1605–1614.

Duinker JC, Schultz DE, Petrick G (1988) Selection of chlorinated biphenyl congeners for analysis in environmental samples. Mar Pollut Bull 19:19–25.

El-Kady AA, Abdel-Wahhab MA, Henkelmann B, Belal MH, Morsi MKS, Galal SM, Schramm KW (2007) Polychlorinated biphenyl, polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran residues in sediments and fish of the River Nile in the Cairo region. Chemosphere 68:1660–1668.

EPA (2002) Reregistration eligibility decision for endosulfan. EPA 738-R-02-013. U.S. Environmental Protection Agency,Washington, DC European Regulation 850/2004/EC (2004) Council Directive of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC (850/2004/EC). Off J Eur Union L158:7–49.

Feng H, Cochran JK, Lwiza H, Brownawell BJ, Hirschberg DJ (1997) Distribution of Heavy Metal and PCB Contaminants in the sediments of an Urban Estuary: The Hudson River. Mar Environ Res 45:69–88.

Fernández MA, Alonso C, Gonzáles MJ, Hernández LM (1999) Occurrence of organochlorine insecticides, PCBs and PCB congeners in waters and sediments of the Ebro River (Spain). Chemosphere 38:33–43.

Frame GM, Cochran JW, Bowadt S (1996) Complete PCB congener distribution for 17 Aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congenerspecific analysis. J High Resolut Chromatogr 19:657–668.

Frignani M, Bellucci LG, Carraro C, Raccanelli S (2001) Polychlorinated biphenyls in sediments of the Venice Lagoon. Chemosphere 43:567–575.

Gatehouse R (2004) Ecological risk assessment of dioxins in Australia–Technical report no. 11. Section 3 Exposure assessment. Department of the Environment and Heritage Australian Government. http://www.deh.gov.au/industry/chemicals/dioxins/report-11/terrestrail.html.

Gomez-Gutiérrez A, Garnacho E, Bayona JM, Albaigés J (2007) Screening ecological risk assessment of persistent organic pollutants in Mediterranean sea sediments. Environ Int 33:867–876 He MC, Sun Y, Li XR, Yang ZF (2006) Distribution patterns of nitrobenzene and polychlorinated biphenyls in water, suspended particulate matter and sediment from mid- and down-stream of the Yellow River (China). Chemosphere 65:365–374.

Hites RK, Day HR (1992) Unusual persistence of DDT in some western USA soils. Bull Environ Contam Toxicol 48:259–264.

HSDB (2003) Hexachlorocyclohexanes. Environmental standards and regulations. Hazardous Substances Data Bank, Bethesda, MD.

HSDB (2007) Heptachlor. Environmental standards and regulations. Hazardous Substances Data Bank, Bethesda, MD

Kim KS, Hirai Y, Kato M, Urano K, Masunaga S (2004) Detailed PCB congener patterns in incinerator flue gas and commercial PCB formulations (Kanechlor). Chemosphere 55:539–553.

Kutz FW, Wood PH, Bottimore DP (1991) Organochlorine pesticides and polychlorinated biphenyls in human adipose tissue. Rev Environ Contam Toxicol 120:1–82.

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

Leaute F (2008) Biogéochimie des contaminants organiques HAP, PCB et Pesticides organochlorés dans les sediments de l'étang de Thau (France). Thèse de Doctorat, Université de Pierre et Marie Curie, Paris, France.

Lee KT, Tanabe S, Koh CH (2001) Distribution of organochlorine pesticides in sediments from Keyonggi bay and nearby areas, Korea. Environ Pollut 114:207–213.

Liu H, Zhang Q, Wang Y, Cai Z, Jiang G (2007) Occurrence of polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls pollution in sediments from the Haihe River and Dagu Drainage River in Tianjin City, China. Chemosphere 68:1772–1778.

MacDonald DD, Dipinto LM, Field J, Ingersoll CG, Long ER, Swartz RC (2000) Development and evaluation of consensus-based sediment effect concentrations for polychlorinated biphenyls. Environ Toxicol Chem 19:1403–1413.

Magnusson K, Ekelund R, Grabic R, Bergqvist PA (2006) Bioaccumulation of PCB congeners in marine benthic infauna. Mar Environ Res 61:379–395.

Mandalakis M, Tsapakis M, Tsoga A, Stephanou EG (2002) Gas–particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). Atmos Environ 36:4023–4035.

Marvin C, Painter S, Williams D, Richardson V, Rossmann R, Van Hoof P (2004) Spatial and temporal trends in surface water and sediment contamination in the Laurentian Great Lakes. Environ Pollut 129:131–144.

Maule A, Plyte S, Quirk AV (1987) Dehalogenation of organochlorine insecticides by mixed anaerobic microbial populations. Pestic Biochem Physiol 27:229–236.

Médail F, Quézel P (1997) Hot-Spots analysis for conservation of plant biodiversity in the Mediterranean Basin. Ann Mo Botan Garden 84:112–127.

Monod JL, Schembri TH, Arnoux A (1987) Evolution des PCB dans un environnement Littoral Méditerranéen depuis la mise en application de l'arrêté Ministériel de Juillet 1975. J Français Hydrol 18:131–139.

Muir DCG, Yarechewski AL (1984) Degradation of methoxychlor in sediments under various redox conditions. J Environ Sci Health B 19:271–296.

Okay OS,Karaik B, Basak S, Henkelmann B, Bernhöft S, SchrammK-W (2009) PCB and PCDD/F in sediments and mussels of the Istambul strait (Turkey). Chemosphere 76:159–166.

Olafdottir OK, Petersen AE, Magnusdottir EV, Brornsson K, Johannesson T (2005) Temporal trends of organochlorine contamination in Black Guillemots in Iceland from 1976 to 1996. Environ Pollut 133:509–515.

OSPAR Commission (2002) Methoxychlor. Hazardous substances series. OSPAR background document on methoxychlor. OSPAR Commission, London, UK, p 22.

Safe SH (1993) Toxic aromatics. In: Kroschwitz JI, Howe-Grant M (eds) Kirk Othmer’s encyclopedia of chemical technology. Wiley, New York, NY, pp 127–139.

Schmidt WF, Bilboulian S, Rice CP, Fettinger JC, McConnell LL, Hapeman CJ (2001) Thermodynamic, spectroscopic and computational evidence for the irreversible conversion of β- to α-endosulfan. J Agric Food Chem 49:5372–5376.

Shaw T (1994) Agricultural chemicals in raw wool and the wool textile industry. J Inst Water Environ 8:287–290.

Senthilkumarl K, Kannan K, Subramanian A, Tanabe S (2001) Accumulation of organochlorine pestiddes and polychlorinated biphenyls in sediments, aquatic organisms, birds, bird eggs and bat collected from South India. Environ Sci Pollut Res 8:35–47.

Shivaramaiah HM, Kenedy IR (2006) Biodegradation of endosulfan by a soil bacterium. J Environ Sci Health B 41:895–905.

Skarphedinsdottir H, Gunnarsson K, Gudmundsson GA, Nfon E (2010) Bioaccumulation and biomagnification of organochlorines in a marine food web at a pristine site in Iceland. Arch EnvironContam Toxicol 58:800–809.

Tang YX, Zou M, Lie HJ, Lie JH (2000) Some features of circulation in the southern Huanghai Sea. Acta Oceanol Sin 22:563–570.

Tolosa I, Readman JW, Fowler SW, Villeneuve JP, Dachs J, Bayona LM, Albaiges J (1997) PCBs in the western Mediterranean.

Temporal trends and mass balance assessment. Deep-Sea Res II Top Stud Oceanogr 44:907–928.

United Nations Environment Program (UNEP) (2006). Persistentorganic pollutants (POPs) http://www.chem.unep.ch/pops.

Vane CH, Harrison I, Kim AW (2007) Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, U.K. Sci Total Environ 374:112–126.

Villeneuve JP, Carvalho FP, Fowler SW, Cattini C (1999) Level and trends of PCBs, chlorinated pesticides and petroleum hydrocarbons in mussels from the NW Mediterranean coast: comparison of concentration in 1973/1974 and 1988/1989. Sci Total Environ 237(238):57–65.

Wafo E, Sarrazin L, Diana C, Schembri T, Lagadec V, Monod JL (2006) Polychlorinated biphenyls and DDT residues distribution in sediments of Cortiou (Marseille, France). Mar Pollut Bull 52:104–107.

Wang F, Bian YR, Jiang X, Gao HJ, Yu GF, Deng JC (2006) Residual characteristics of organochlorine pesticides in lous oils with different fertilization modes. Pedosphere 16:161–168.

Wang H, He M, Lin C, Quan X, Guo W, Yang Z (2007) Monitoring and assessment of persistent organochlorine residues in sediments from the Daliaohe River watershed, Northeast of China. Environ Monit Assess 133:231–242.

Yamashita N, Urushigawa Y, Masunaga S, Walash MI, Miyazaki A (2000) Organochlorine pesticides in water, sediment and fish from the Nile River and Manzala Lake in Egypt. Int J Environ Anal Chem 77:289–303.

You J, Schuler LJ, Lydy MJ (2004) Acute Toxicity of Sediment-Sorbed Endrin, Methoxychlor, and Endosulfan to Hyalella Azteca and Chironomus tentans. Bull Environ Contam Toxicol 73:457– 464.

Zhang P, Song J, Liu Z, Zheng G, Zhang N, He Z (2007) PCBs and its coupling with eco-environments in Southern Yellow Sea surface sediments. Mar Pollut Bull 54:1105–1115.

Zhang XL, Luo XJ, Liu J, Luo Y, Chen SJ, Mai BX (2011) Polychlorinated biphenyls and organochlorinated pesticides in birds from a contaminated region in South China: association with trophic level, tissue distribution and risk assessment. Environ Sci Pollut Res 18:556–565.

Zhao L, Hou H, Zhou YY, Xue ND, Li HY, Li FS (2010) Distribution and ecological risk of polychlorinated biphenyls and organochlorine pesticides in superficial sediments from Haihe River and Haihe Estuary Area, China. Chemosphere 78:1285–1293.

CHAPTER V

FATE AND OCCURRENCE OF ALKYLPHENOLS (APs) IN COASTAL AREA OF CORTIOU CREEK, THE BAY OF MARSEILLES.

Halikuddin UMASANGAJI, Agung Damar SYAKTI, Laurence ASIA, Fehmi KANZARI, Laure MALLERET, Yann TERNOIS, Pierre DOUMENQ

SUMMARY

The Alkylphenols solely derive from anthropogenic activities and are recognized massively, particularly in the marine environment. These ubiquitous substances are chategorized as endocrine disrupting compounds, mutagenic and are able to induce adverse effects to the marine ecosystem due to their ability to mimic the natural hormones. Additionally, marine sediments are widespread to be excellent traps for pollutants such as Alkylphenols.. There were numerous works that have been carried out throughout the globe assessing the concentrations of these APs in the different environmental matrices not only in sediment, but also in water, soil, even air and foods. Nonetheless, there were very little studies focused on the dynamic of these chemicals throughout the plume at the estuarine area or the outfall of WWTPs and how they respond under several physico parameters such as wind, currents and some geochemistry factors. These are the essential constituents that play the important roles in terms of fate and occurrence, distribution patterns of organic micro pollutants in the littoral area, both in short and long terms.

In this fifth chapter, which corresponds to the concentration levels of these compounds, particularly in sediment, soil and the most explorative one namely aerosol, research was carried out in the Cortiou Creek of Marseilles. We will first describe the magnitude of APs, especially the three commercials of these organic micro-pollutants (4-tert-OP, 4-n-OP and the three isomers of NPs namely NP$_1$, NP$_2$ and NP$_3$) which occur in sediment, soil and aerosol. We will also attempt to determine their relationship with total organic carbon (TOC) and particle sizes which play a necessary role in adsorbtion processes of organic materials. We have also assessed the environmental risk by employing Predicted No-Effect Concentration (PNEC).

The dissemination of NP$_1$, NP$_2$ and NP$_3$ in sediments at the 8 stations directly connected to the emissary point of WWTPs ranged from 30.3 to 100 µg.kg^{-1} (62.93±40.97), 11 to 60.82 µg.kg^{-1} (28.09±16.91), 58 to 216.5 µg.kg^{-1} (117.58±60.30), respectively. Whereas, 4-n-OP was detected from 2.08 to 3.72 only at the station P1, P4 and P11, 4-t-OP was not detected. Subsequently, the stations were beyond WWTP's outfall, these compounds ranged from 13.1 to 75 µg.kg^{-1} (33.67 ± 23.73), 1.68 to 24.24 µg.kg^{-1} (11.11 ± 7.41), 9.3 to 55.89 µg.kg^{-1} (23.89±16.78), respectively. Furthermore, 4-n-OP and 4-t-OP were barely found in station P14. The highest concentrations were NP$_1$ and NP$_3$ compared to NP$_2$. Whereas 4-n-OP and 4-t-OP were discovered in very discrete concentrations. Statistically, we found that there was no correlation between APs and TOC, particle sizes and geochemistry elements which were unexpected. These findings suggest that there were other factors that have equal or greater contributed to the sorbtion and distribution of these compounds.

Interestingly, the majority of the stations in the east side have the highest concentrations compared to other stations in the west which is proof that 85% of plume deflection towards the east side of the site is due to the prevailing wind direction, turbulence and upwelling dynamic in this coastal ecosystem.

These chemical concentrations in soil samples at the four stations exposed to the prevailing wind, collected at the stations of the Cortiou Creek show NP$_1$, NP$_2$ and NP$_3$ varied from 21.32 to 81.87 µg.kg^{-1} (48.08±27.70), 14.42 µg.kg^{-1} to 29.47 µg.kg^{-1} (19.49 ± 6.92), and 142.97 µg.kg^{-1} to 461.12 µg.kg^{-1} (339.13 ±138.26),

respectively. Whereas, 4 n OP was nd to 80.45 µg.kg^{-1} only at the stations S1 and S3, 4 t OP detected barely at station S3. Furthermore, the stations are protected from the valley, NP_1, NP_2 and NP_3 were detected from 6.2 to 12 µg.kg^{-1} (9.1 ± 4) , 3.13 µg.kg^{-1} to 8.56 µg.kg^{-1} (5.8 ± 3.84), and 28.83 µg.kg^{-1} to 54.00 µg.kg^{-1} (44.41±17.80), respectively. A measurement of 4 n OP was scarce at station 5 with a result of 44.65 µg.kg^{-1} while 4-tert-OP was undetectable. It is suggested that the stations are influenced by southeast wind which contributes higher concentrations of APs in surface soil than that of the protected ones. Meanwhile NP_3 was appeared to be the prominent isomer throughout the stations. The emissary point of WWTPs presumably plays an important role in contributing the residues of APs both in marine sediments and soil samples. Unlike in sediments, we found that these APs have a significant correlation with TOC which explained that the sorption of these contaminants in surface soil was controlled by organic carbons in this marine environment.

Moreover, to the best of our knowledge, this is the first study of these pollutants in aerosol matrice in this coastal area directly connected with the outfall of WWTPs. The measurements of the three isomers of NPs (NP_1,NP_2 and NP_3) concentrations in the air were classified in five different sizes, namely > 72 µm, 3 – 7.2 µm, 1.5 – 3 µm, 0.92 – 1.5 µm, 0.49 – 0.96 µm ranged from 1 to 3.95 ng.m^{-3}, 0.61 to 1.16 ng.m^{-3}, 1.32 to 13.91 ng.m^{-3} respectively. Similar to sediments and soil, NP_1 and NP_3 were the predominant isomers found in this matrice. Whereas, 4-n-OP and 4-tert-OP were not detected in aerosol samples. The most elevate concentrations of NP_3 occurred in a particle size of 0,92 to 7,2 µm which are well-categorized as primary marine aerosols (PMA) as suggested by Clarke *et al* 2006 ; Nilsson *et al* 2001 and Geever *et al* 2005. These particle modes were the majority derived from sea salt (Grass and Ayers 1983). On the other hand, we also found a particle size with $r < 0,25$ µm as a fine mode particle which is predominantly of non-sea salt sulphate (nss-sulphate).

In order to determine whether these compounds derived from the same sources or not, we quantified the ratios between NP/AP. The indices show the similar values for these different matrices (sediment, soil and aerosol) as summarized in Table 5.20. The ratios of NP_1 in sediments ranged from 0,13 to 0,53 with arithmetic mean of 0.29, while soil samples were observed of 0,07 to 0,16 with an arithmetic mean of 0,12. The aerosols matrice provides 0,10 to 0,36 with arithmetic mean of 0,23, respectively. Concerning NP_2 isomer, their contribution in sediments ranged between 0,09 to 0,16 with an arithmetic mean of 0,13, while soil samples provide 0,02 to 0,08 with arithmetic mean of 0,08 and aerosols contributed as 0,04 to 0,36 with arithmetic mean of 0,15. Concerning NP_3, the sediment samples provide 0,37 to 0,73 with arithmetic mean of 0,58, while we found soil samples of 0,45 to 0,88 with an arithmetic mean of 0,58. The contribution from aerosols was observed at 0,45 to 0,88 with an arithmetic mean of 0,67 respectively. These diagnoses suggested that these matrices have several similar ratios of each isomer to APs which implies that they might have been derived from the similar sources at the same period of input.

Moreover, to diagnose the environmental significance of APs, we compared our data with consensus based sediment and soil guide lines (PNEC, Predicted Non-Effect Concentration) (INERIS, 2014 ; European Commission, 2002). Through these conventions, the results suggest a potential adverse effect on marine biota (>39 µg.kg^{-1} dw) due to the majority of the sediment samples (62,92%) which exceeded the PNEC value. Regarding soil samples, the concentrations of APs ranged from 3,13 to 396,8 µg.kg^{-1} dw with the maximum concentrations being found at stations S1, S2 and S3 which were situated at the corridor exposed to the predominantly high wind direction. 16% of NPs isomers in the soil samples in this coastal zone exceeded PNEC (300 µg.kg^{-1} dw). These findings indicate that there is an adverse effect towards organisms in the vicinity of the Cortiou Creek. Accordingly, the sediment and soil of the Cortiou Creek, can be speculated that the study area carries an ecological risk. Nonetheless, Roberts et al 2006 discovered that these ranges of pollutants in soil could not pose any negative risks to the plants and organisms in this area unless the magnitudes of these chemicals exceed 10,000 mg.kg^{-1} dw. These concentrations of NPs can be transported from the soil to the surrounding animals and plants. Additionally, it was suggested that the uptake of NP by plants is very low refering to these values. When NPs are adsorbed to the solid phase, they could easily be leached from soil. Taking all of our results in to account, we conclude that the spreading of NPs in soil, probably does not pose any environmental risk to the terrestrial ecosystems and human health.

This research indicates that the most deposited APs was in soil which attribute that the final depsited of these substances is presumably in soil after having had some physical and chemical processes in other mediums such as water, sediment and air.

Even though the new WWTPs-cleansing unit (Géolide) has been implemented with the last generation’s process of biological treatment, this work suggests that adverse effects linked to NPs abundance probably happened in sediments and potentially in soils. However, considering first, that the surficial sediments integrate a large time span, and second, the technical difficulty to obtain sediment cores in this area, it is too early to see the positive effects of the WWTP biological process and it is difficult to predict when this improvement can be highlighted. Hence, in the future, it is necessary to regularly monitor the contamination of soils and sediments in the vicinity of the WWTP.

This article is being prepared to published in "International Journal of Environmental Science and Technology" as a summary of the main work done in this study. It became significant from this information for further study in accompany with the analysis of the concentrations levels in biota, water and the oceanography parameters measurement which could allowed to create a model. This would be expected to be an explanation of some physical information which led us to describe the distributions profile of these compounds related to the several physical parameters. Since the deviation of the plume eastward still remains a question.

Fate and Occurence of Alkylphenols in Coastal Area of Cortiou Creek, The Bay of Marseilles

Halikuddin UMASANGAJI, Agung Damar SYAKTI, Laurence ASIA, Fehmi KANZARI, Laure MALLERET, Yann TERNOIS, Pierre DOUMENQ

Abstract

Multiplication of anthropogenic influences in the littoral ecosystems necessitates use of an integrated assessment strategy for effective interpretation and subsequent management. In this study, the concentration levels of Alkylphenolic (APs) compounds were measured and quantified in sediments, soil and aerosols collected in the vicinity of Cortiou Creek, coastal area of Marseilles directly connected to the Wastewater Treatment Plant (WWTPs). The three isomers of NPs (NP_1, NP_2 and NP_3) were detected in sediments throughout the plume with averages at each station of 62.93 µg.kg^{-1}, 28.09 µg.kg^{-1}, 117.58 µg.kg^{-1} respectively. Whereas, 4-tert-Octylphenol and 4-n-Octylphenol were detected in discrete concentrations. The stations beyond the plume measured 33.67 µg.kg^{-1}, 11.11 µg.kg^{-1}, and 23.89 µg.kg^{-1} respectively. Furthermore, these chemicals were found largely in soil samples with average amounts of each isomer distributed in 6 stations at amounts of 48,08 µg.kg^{-1}, 19.49 µg.kg^{-1} and 339.13 µg.kg^{-1} exposed to the prevailing wind, while at the stations protected by the predominantly high wind, the concentrations ranged between 5.8 µg.kg^{-1} and 41.41 µg.kg^{-1}. The most explorative one is the occurrence of these APs in aerosol samples which were detected from 0.81 to 8.46 ng,m^{-3}. Meanwhile, 4 tert OP and 4 n OP were undetected in these samples. The most elevated isomers found from this study were NP_1 (28.44%) and NP_3 (57.54%) within three different matrices. Through the analysis of the ratios among these substances, these chemicals were presumably derived from the same sources either directly from the emissary point of WWTPs or input from other activities such as shipping traffic and domestic discharge. The coefficient correlation between TOC, particle sizes and APs concentrations in sediments and soils shows uncorrelated results which were unexpected. These findings suggested that these organic compounds were probably allochthonous. Parallel, particle sizes and geochemistry factors such as Al, Li and Pb contributed a slight positive correlation which means that beside the influences of these elements, there were probably other constituents equal to or of greater importance to the settelment of these substances in the Cortiou Creek area.

Regarding the dynamic of the plume emitted by WWTPs outfall, the flow deviates to the southeastward of the study area as the influences of the prevailing wind, turbulence and the intensive upwelling phenomenon takes place at this site. These processes have likely made the pollutants more concentrated at the southeastern side of the plume.

According to the Predicted No-Effect Concentrations (PNEC), these concentrations in the sediments exceeded the PNEC value which means they probably pose an adverse effect to the benthic organisms. On the other hand, in soil, these APs concentrations do not have any impacts to the plants and human health in the vicinity of Cortiou. Overall, this research indicated that the most stored APs was in soil. The final deposite of these substances is presumably in soil after having had any physical and chemical processes in the other mediums such as water, sediments and air.

Key words : Alkylphenols, WWTPs, sediments, soils, arosols, PNEC, adverse effect, allochthonous

5.1. Introduction

Anthropogenic activities such as urban, agriculture, industrial and wastewater treatment plant (WWTPs) have been emitting a large number of pollutants that induced high risk not only towards marine organisms but also human health, particularly endocrine disrupting compounds (EDCs) which may alter the development, growth, reproduction and behavior of human beings and several organisms at very low concentrations (Zhang *et al* 2011 and Salguiero-Gonzalez *et al* 2016).

The extensive emission of these EDCs such as APs and LABs is the product of primary microbial degradation of APEOs and LAS into sea surface water via the discharge of treated and treated

WWTPs. This has been fascinating work by scientists who have investigated their existents and impacts to marine ecosystems (Daughton and Ternes 1999; Kolpin *et al* 2002; Fent *et al* 2006; Khetan and Collins 2007; Berninger and Brooks 2010; Bruce et al 2010; Klosterhause *et al* 2013). The most important commercial APs are Nonylphenols (NP) and Octylphenols (OP) that have been continuously applied in the production of nonionic surfactants (alkylphenol ethoxylates, APEOs) since the 1940s (White *et al* 1994; Duan *et al* 2014). Both Nonylphenol polyeothoxylates (NPEOs) and octylphenol polyeothoxylates (OPEOs) approximately reached 80% and 20% of the total APEOs (Ying et al 2002; Duan *et al* 2014). Meanwhile, annually, general manufacture of these substances exceeded 500,000 tons in 1997 (Ying *et al* 2002; Duan *et al* 2014), and this manufacture will extensively increase in the coming years.

Since the emission of WWTPs and garbage are being dumped directly into the marine ecosystem along with a great deal of sewage and garbage being increasingly drained into the sea (Hawrelak *et al* 1999; Céspedes *et al* 2008; Duan *et al* 2014), the biggest part of APEOs is released towards the environment and eventually ends up into the sea (Renner 1997; Solé *et al* 2000; Duan *et al* 2014). These substances are freely movable in the marine environment with a half-life of a few days and will degrade to alkylphenols (AP) via bio- and photo-degradation (Li *et al* 2013a).

Nevertheless, NP and OP are much longer stable in the environment with a half-life of a few decades in the sediments either marine or fresh water ones (Isobe *et al* 2001; Duan *et al* 2014). Hence, NP and OP are ubiquitous in the general environment which many evidence presence their occurrence in sediments (Uguz *et al* 2003; Fiedler *et al* 2007; Klosterhaouse 2013; Duan *et al* 2014; Lee *et al* 2018) in soil (Andreu *et al* 2007; Jimenez-Diaz *et al* 2010; Padilla-Sanchez *et al* 2010) in water (Munaron *et al* 2012; Devier *et al* 2013; Ciofi *et al* 2014; Pernica et al 2015; Priac *et al* 2017) in air (Spiel *et al* 1996; Xie *et al* 2006; Laborie *et al* 2016) and biota (Klosterhouse *et al* 2013; Salguiero-Gonzalez *et al* 2016; Staniszewska *et al* 2017; Ismail *et al* 2018).

The occurrence of these chemicals in the littoral zone induces adverse biological impacts such as feminization of male fish and the alteration of reproductive organs development. The problems that probably occur possed by these endocrine disrupting in aquatic ecosystems has been attracted a numbers of works throughout the globe (Hosokawa *et al* 2003; Braga *et al* 2005; Vethaak *et al* 2005; Pojana *et al* 2007; Tan *et al* 2007; Bjorklund *et al* 2009; Sharma *et al* 2009; Ying *et al* 2009; Zhang *et al* 2009; Arditsoglou and Voutsa 2012; Gong *et al* 2011; Saeed *et al* 2017).

Since their harmfull effects and toxicity in the environment, the application and manufacture of such substances have been banned or strictly monitored in many countries (Duan *et al* 2014; Saeed *et al* 2018). OSPAR established APs in the priority list of compounds that are toxic to marine organisms (Maguire 1999). These substances are also part of the list of 33 priority substances determined by the European Water Framework Directive (Directive 2008). They are also listed in the "List of Undesirable Substances" (LOUS 2009, 2011) of the Danish Ministry of the Environment. Moreover, APs were included in the list of 45 priority substances in the water policy under the Directive 2013/39/EU. The US EPA has strictly restricted the amount of APs in various industrial products (Huang *et al* 2016; Saeed *et al* 2018). The lack of data on these compounds, their priority character and the high probability of discovering them in the study area (emissary point of the Cortiou wastewater treatment plant) lead us to study sistematically in this work.

Marseilles city has a large various biodiversity particularly in the littoral zone as part of typical Mediterranean's richness. One of the most eco-touristic well-known is Cortiou Creek where is heavily impacted by sewage derived from Marseilles and several suburbs. The coastal with high risk polluted area in French Mediterranean from the various sources such as domestic, agricultural activities, harbor maritime and industrial activities. The sewage contributed of 250,000 $m^3.day^{-1}$ of their output which is principally carried westward by the currents and prevailing winds. This sewage was untreated until 1987 and has been treated only by a primary plant (chemically assisted sedimentation) to 2008. By this time, this WWTPs is chategorized as one of the largest in the world (1,860,000 inhabitant-equivalent) (Lardy-Fontan 2008, *thesis unpublished*; Robert-Peillard *et al* 2015) firstly employed physic-chemical procedure including solid removal and chemical-assisted (flocculation/coagulation) sedimentation followed by a secondary biological treatment based on the biostyr system. The secondary-treated sewage produced a daily average flow rate of 2,9 $m^3.s^{-1}$ (by dry weather) to the Cortiou Creek.

To date, many works have been carried out in this area to determine the concentrations levels of alkylphenols and alkylphenols polyethoxylates (Lardy-Fontan 2008, unpublished ; Robert-Peillard *et al* 2015), linear alkylbenzene and linear alkylbenzene sulfonate in water samples (Robert-Peillard *et al* 2015). However, it still remains the particularly zone at Cortiou area and the behaviour of these contaminants influenced by the hydrodynamic factors. This is the interesting thing that has not been determined by other works thus our present work tried to investigate the concentrations level of those contaminants within the three different compartments, their fate and also how they interact to the several physical factors in this polluted zone. The potential of environmental risk and their temporary trend are being assessed as well.

5.2. Material and Methods

5.2.1. Description of Study Site

The inshore of South East France and Var departments in France are well-known for their rich multifariousness and environmental essence (Abucaya *et al* 2001). This biogeographical area is part of ten biodiversity with a place of significant activities in the Mediterranean Basin (Medail and Quezel 1997). So as to better mitigate, protect and conserve against anthropogenic impacts, 'Calanque National Park'has been established in 2012. This region located in Southern France which extends over 520 km^2 of which 85 km^2 is land, while the remining is marine area. This is the the first suburban nationa park in Europe. It includes parts of the Massif of Calanque stretching between Marseilles and Cassis. We have chosen our study site at the center of the Calanque National Park encompasses the Friou archipelago, plane, the Marseilleveyre Islands and Cap Croisette up to Green Island where the potential pollutants of the marine environment particularly derived from treated urban wastewater discharged at a rate of up to 280,000 m^3 each day. This includes used water from Marseilles and its suburbs, a population of at least 1.8 million people. Other potential persistent organic pollutants (POPs) derived from Marseilles and the Huveaune River, particularly during intense rainfall, can be by passed through the Cortiou messenger. In 2008, Marseilles authorities upgraded their wastewater treatment plan 'Géolide' by integrating a biological treatment which considerably reduce the impact of urban organic pollutants on the marine environment but did not entirely resolve the problem of some emergent pollutants such as Alkylphenols. This study was undertaken within the framework of the French National Research Agency (ANR) program MARSECO.

5.2.2. Sample Collection

As shown in Figure 5.1, samples from 8 stations (three independent subsamples per station) were collected from sewage outfall of the wastewater treatment plant of Cortiou – Marseille, France. Surface sediment samples were collected on 21st March and 23rd June 2010 with a sediment grab sampler (Shiptex ; Wildco, USA) and PVC core samplers (Ø 100 mm) using SCUBA equipment.

The sampling points lie perpendicularly to the coast line (237ºN) starting from the sewer outlet to the seaward. All sediments samples were freeze-dried, then sieved using a 2 mm mesh, homogenized and stored at -18ºC prior to analysis.

Concerning soil samples, after removal of the superficial litter, the most superficial horizon was determined and then manually sampled with metal tools. Soils were then homogenized, sieved to 2 mm and then preserved as sediments.

5.2.3. Chemicals

4-tert-Octylphenol, 4-n-Octylphenol and 4-Nonylphenol technical (NP_1, NP_2 and NP_3) were purchased from Dr. Ehrenstorfer. The standard solutions were prepared in methanol. The analytical grade solvents used such as diethyl ether, methanol, dichloromethane were purchased from VWR International (Fontenay Sous Bois, France). Acenaphtene as internal standard was obtained from Sigma Aldrich, France. The 3 mL of 200 mg of Chromabond HR-X SPE sorbent cartridges were purchased from Macherey-Nagel (France).

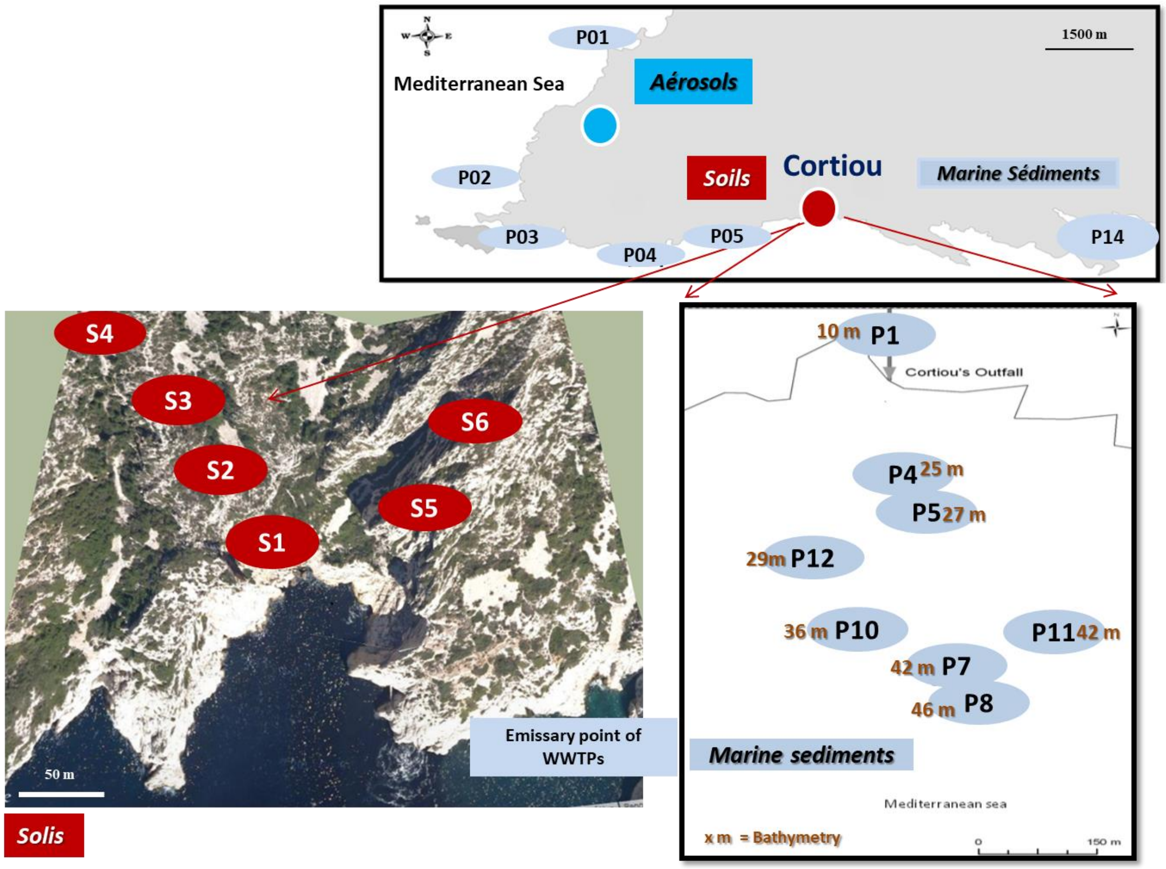


Figure 5.1. Study site and sampling location

5.2.4. Sample preparation

5.2.4.1. Sediments and soils

Pressurized liquid extraction

All the glassware was washed and then heated at 300°C for 12 hours prior to use. Ten gram of dried solids samples were placed in a cylindrical glasses cells and extracted using a Soxtherm Solvents Extractor (Model Gerhardt type Multistat 50 – 60, Germany). Each extraction began with 4 min preheating time followed by 5 min heating and then 5 min static extraction with methanol. The static extraction was performed at constant temperature (120°C, 6900 kPa), 2 cycles extraction was used. The extract (~45 ml) was reduced using rotary evaporation to less than 35 ml then top up to 35 ml with methanol and finally placed into 100 mL calibrated flask and top up to 100 mlwith water (Jimenez-Diaz *et al* 2010).

Solid-phase extraction

The analysis processing is described in details elsewhere (Jimenez-Diaz, 2010) with minor modification. Briefly, the extract underwent SPE on an Isolute ENV + Cartridge previously activated with diethyl ether (5 ml), methanol (5 ml) and water (5 ml). The extracts (100 ml) were passed through the cartridges at a flow rate 2 – 3 ml.min^{-1}. The first fraction elution for a clean-up procedure and was performed by passing 5 ml of methanol/water 20:80(v/v) and then the cartridge was dried under vacuum for 15 min. Second fraction containing the targeted compounds, was performed with 5 mL of diethyl ether/methanol 90 :10 (v/v). Elution were evaporated to dryness at room temperature under a stream of nitrogen.

Furthermore, 250 µl dichloro methane containing 20 µl of acenapthene as internal standard and 40 µl of BSTFA/TMCS 90:10 (v/v) were added to the vial in order to carry out the redisolution and the derivatization of the residue. Next, vials were closed, heated at 50°C during 5 min to complete the derivatization process. After this reaction, 2 µl of the product was injected into GC-MS system.

Gas-Chromatographic analysis

The quantitative analysis of APs were carried out using a Gas Chromatograph (GC) equipped with a GC auto-sampler, split/splitless injector and coupled with a mass spectrometer (Perkin-Elmer Autosystem XL, California, USA). The separation was achieve with a fused silica capillary column (Elite-5MS, 30 m x 0,25 mm ID with 0,25 µm thickness film Perkin-Elmer, California, USA). The oven temperature was programmed to increase from 85 – 130°C within 10°C.min^{-1} and increased to 300°C at 6°C.min^{-1} held for 2,5 min. The injector was set at 300°C and the MS source at 230°C.

5.2.4.2. Aerosols

Regarding aerosol, we used a high volume (1000 m^3) cascading impactor by placing near to Col de Moute, west of Cortiou. As this point is well exposed to the prevailing wind from southeast and under the influence of emissary point of WWTPs.

This instrument dedicated to the analysis of marine aerosols that was equipped with 5 separate sampling stages allowing to aerodynamically separate the aerosol in 5 size classes ranging from 0.49 to 7.2 µm and more (Figure 5.2).

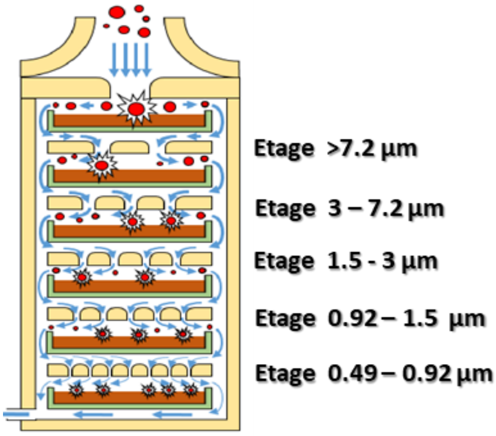


Figure 5.2. Multistage cascade impactor

Prior sampling, quartz fiber filters were pre-cleaned by heating in an oven at 800°C for 8 h. Mass concentrations were obtained gravimetrically using an electronic microbalance with a readability of 1 µg (Mettler Toledo, model X5) in a controlled atmosphere room where filters were equilibrated for 24 h prior weighing. Extraction, purification and identification were carried out in the same method as committed to sediments and soils.

5.2.5. Granulometric Analysis

Sediment samples were prepared from AR grade calcium carbonate (minimum 99.5% $CaCO_3$). This was ground for fifteen minutes using a glass pestle and mortar to breakdown any aggregated that may have formed during storage. Approximately 10 gram of samples was removed to a small porcelain crucible and 'Calgon'solution added one drop at a time until a thick plastic paste formed. Dry samples are not particularly suited to particle size analysis – they tend to show distinct grain size sorting, leading to problem in accurate sub-sampling.

Particle size was measured using a Beckman-Coulter LS 230 laser particle size analyzer, equipped with a fluid module. This uses a 5mW, 750 nm laser beam and 126 detectors placed at a range of angles up to 35° to the laser beam. The LS 230 measures particle sizes in two ways, using the Fraunhofer and Mie theories of light scatter.

Conventional (Fraunhofer) laser diffraction is used to measure particle in size range 2 mm to 0.4 µm. The Fraunhofer theory relies on the fact that when light from a laser is shone at a particle, some of it is diffracted. The amount of diffraction is dependent upon the size of the particle. The smaller the particle, the greater the maximum angle of diffraction. Thus, particle of different sizes each produce a characteristic diffraction pattern.

A second unit measures particle size down to 0.04 µm using a proprietary technique that Coulter refer to as PIDS (Polarisation Intensity Differential Scatter). This is also based on laser diffraction, but measures light flux only at high angle to the beam. Using six detector and tungsten light sources, the PIDS unit compares the intensity of light scatter at two polarization angles, at three different wave lengths (450, 600 and 900 nm), allowing measurement in the range 0.04 – 2000 µm. Measuring the size of a single particle in this way is relatively simple, but measuring a mixture of particles of different sizes requires mathematical modeling. The LS 230 applies a user-specified optical model to distinguish between the signals from each particle in the sample. The model is applied post-measurement, so that the choice at analysis time is not critical.

Interpolation of the LS230 output was carried out using version 3.01 of the Coulter LS Control Software. Statistical analysis of the resulting data was carried out using Minitab version 11.

5.2.6. Minor and trace elements analysis

These data were collected by Oursel et al 2014 under permitted by the authors.

Particulate elements (Al, Li and Pb,) were quantified from the acid-digested filters by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS Element 2, Thermo Finnigan). The instrument was calibrated using standard solutions and an In was added as internal standard in each sample (Lenoble *et al* 2013). Quality control of HR ICP-MS measurements was checked by the determination of elements concentration on Certified Reference Material (SLRS-4 river water, LGC6187 river sediment, National Research Council Canada). All results presented good agreement with the certified data. Results obtained for LGC6187 (triplicate) showing that the values obtained for most of the studied elements fall in 90 - 110% of yield.

5.2.7. Quality control

APs compounds were extracted using soxtherm with methanol as solvent. Before extraction, acenapthen as an internal standard was spiked to the samples. The results revealed that the mean recovery values are (4-t-OP = 94.35%), (NP_1 = 101.5%), (NP_2 = 90%), (NP_3 = 115%) (4-n-OP = 94%). This indicates that the analytical procedures were reliable, reproducible and efficient. Appropriate corrections were made to the measured concentrations. Procedural blanks as well as solvent blanks were analyzed and quantified to ensure that there were no significant background interferences, no APs compounds of interest were detected in these blanks.

5.3. Result and Discussion

Sediments

5.3.1.1. Spatial evolution of Alkylphenols (APs) concentrations in Cortiou creek.

Total APs concentrations distributed within four-teen stations of marine sediments were shown in Table 5.1 and Figure 5.3. Concerning Cortiou stations (Table 5.1.A) APs levels were measurable between 79.3 to 377.32 µg.kg^{-1} with arithmatic mean of 209.65 µg.kg^{-1}. These values were accompanied by total organic carbons (TOC,%) which were ranged between 0.8 to 8.8% with arithmetic mean of 3.3%. The highest concentration was occurred at station P5 at the distance of 300 m from emissary point of WWTPs. While the lowest one took place at station P12 at the distance of 380 m at the western side of the plume. Interestingly, the stations situated at the western side of the plume (P10 and P12) have the lowest level of APs compared to the eastern side (P5 and P11). Subsequently, the out side of Cortiou stations (Table 5.1.B) recorded the concentrations of total APs went from 24.08 to 129.50 µg.kg^{-1} with arithmetic mean of 69.44 µg.kg^{-1}. The highest concentration was found at station P14 at the distance of 3.67 km from emissary point and the lowest one was occurred at station P04 at the distance 2.9 km from emissary point. This finding attributed to the fact that the persistence and ease of transport of these anionic surfactant substances. This result is in a good agreement with those reported by Robert-Peillard *et al* 2015 found the same distribution pattern in water at the same study site. However Robert-Peillard found only NPEO in water sample in this environment, while NP was not detected. Comparing to our recent work at the same site which are found NP in high amount within sediments (208.58 µg.kg^{-1}) suggested that these substances were more soluble in sediment matrices than in the waters as their high log K_{ow} (4.48) and hydrophobicity.

Table 5.1. The distribution of APs (µg.kg^{-1}) concentrations and TOC (%) in Cortiou creek and outside of Cortiou creek stations .

(A)	**Coordinate position**		**Cortiou stations**						
Stations	**Longitude**	**Latitude**	**NP1**	**NP2**	**NP3**	**4-n-OP**	**4-t-OP**	**∑APs**	**TOC(%)**
P1	43°12’44.58’’	5° 24’ 11.28’’	130	22.2	90.06	2.68	nd	**244.94**	1.9
P4	43°12’39.66’’	5° 24’ 12.18’’	40.4	19.75	**139.55**	3.72	nd	203.42	2.6
P5	43°12’37.8’’	5° 24’ 12.66’’	100	60.82	**216.5**	nd	nd	**377.32**	1.7
P12	43°12’34.69’’	5° 24’ 8.47’’	10.53	11	58	nd	nd	79.53	1.6
P10	43°12’30.27’’	5° 24’ 10.29’’	32.1	17.18	59.85	nd	nd	109.15	1.3
P11	43°12’29.93’’	5° 24’ 18.11’’	83.58	34.59	**140.5**	2.08	nd	**260.75**	0.8
P7	43°12’27.36’’	5° 24’ 14.16’’	76.52	43.17	**177.33**	nd	nd	**297.02**	7.4
P8	43°12’25.98’’	5° 24’ 14.76’’	30.3	16.03	58.82	nd	nd	105.15	8.8
Total			**503.43**	**224.74**	**940.61**	**8.48**	**0**	**1677.28**	**26.10**
Average			62.93	28.09	117.58	2.83	0	209.66	3.26
Stadeva			40.97	16.91	60.30	1.53	0	105.28	3.05
(B)	**Coordinate position**		**Cortiou stations**						
Stations	**Longitude**	**Latitude**	**NP1**	**NP2**	**NP3**	**4-n-OP**	**4-t-OP**	**∑APs**	**TOC(%)**
P01	43°14’57.11’’	5° 21’ 51.3’’	18.65	10.08	26.06	nd	nd	**54.79**	NA
P02	43°13’4.65’’	5° 20’ 37.47’’	15.4	12.5	22.08	nd	nd	49.98	NA
P03	43°12’29.27’’	5° 22' 20.02’’	13.1	1.68	9.3	nd	nd	24.08	NA
P04	43°12’20.12’’	5° 22’ 5.26’’	75	8.04	13.48	nd	nd	**96.52**	NA
P05	43°12’30.9’’	5° 23’ 4.57’’	35.16	10.1	16.52	nd	nd	**61.78**	NA
P14	43°12’33.62’’	2° 26’ 58.61’’	44.71	24.24	55.89	1.77	2.89	**129.5**	NA
Total			**202.02**	**66.64**	**143.33**	**1.77**	**2.89**	**416.65**	0
Average			33.67	11.11	23.89	0	0	69.44	0
Stadeva			23.73	7.41	16.78	0	0	37.55	0

These concentration values (Table 5.1 A and B) were obtained with a method precision assessed by replicate injection of standard solution (n = 6) expressed as the relative standard deviation (RSD). RSD on the calculated concentrations of the replicates was less than 15%.

APs = Alkylphenols, NP = Nonylphenols, OP = Octylphenol, TOC = Total organic carbon, NA = Not analyzed.

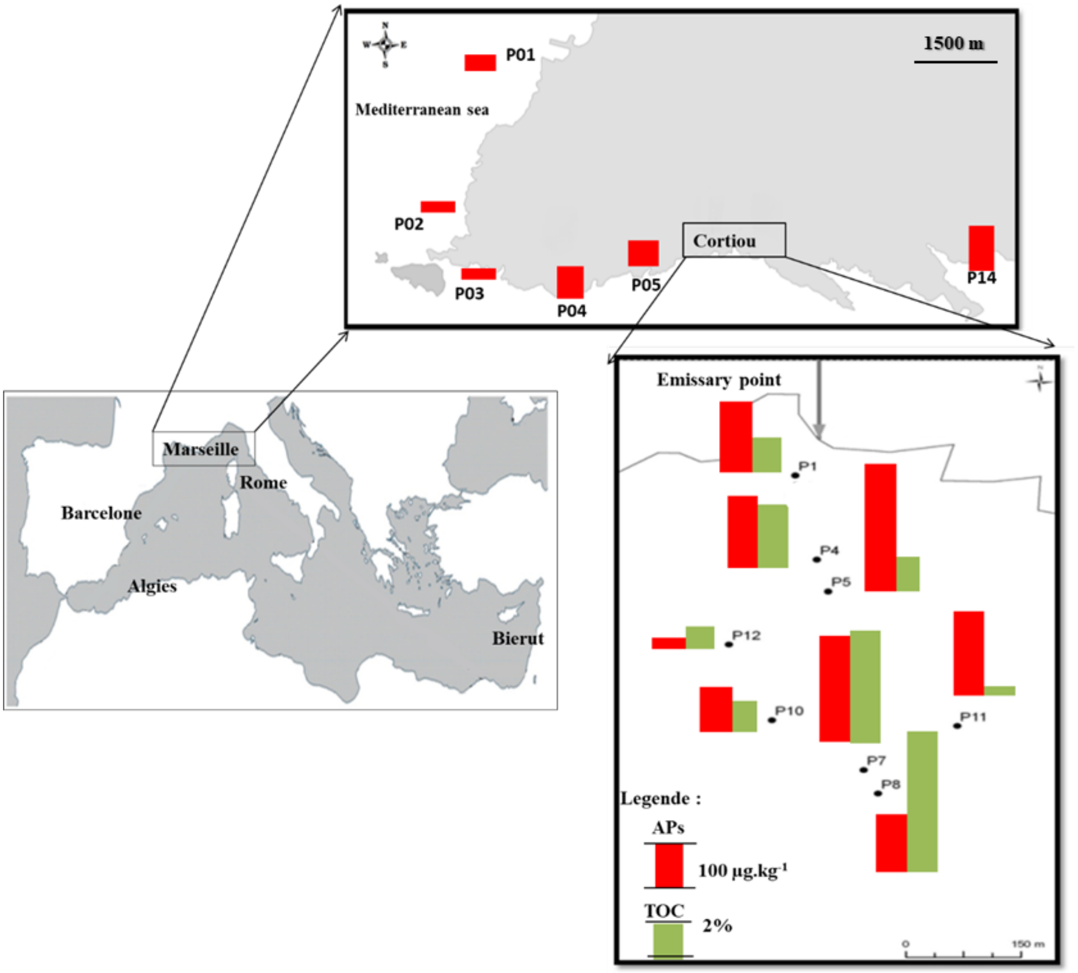


Figure 5.3. The distribution of APs (Total Alkylphenols) and TOC (Total organic carbon) as a function of the distance from emissary point of WWTPs.

Each APs analyzed were NP, 4-n-OP and 4-tert-OP that distributed and summarized in Table 5.1. Concerning the Cortiou stations presented NP1 of 30.3 to 130 µg.kg^{-1} with arithmetic mean of 62.92 µg.kg^{-1}, NP$_2$ of 11 to 60.82 µg.kg^{-1} with arithmetic mean of 13.44 µg.kg^{-1} and NP3 of 58 to 216.5 µg.kg^{-1} with arithmetic mean of 117.57 µg.kg^{-1} respectively. Subsequently, 4-n-OP was only detected at the stations P1, P4 and P11 which was ranged between 2.08 to 3.72 µg.kg^{-1} with arithmetic mean of 2.82 µg.kg^{-1}. On the other hand, 4-tert-OP was not detected (nd) in this area (the values were below LOD of 1.5 µg.kg^{-1}). These concentrations were accompanied by the percentage of Total Organic Carbon (TOC) in Cortiou Creek surface sediments that was measurable between 0.8 to 8.8% with arithmetic mean of 3.3%. Concerning the outside of Cortiou stations, the concentrations of NP$_1$ ranges between 13.1 to 44,71 µg.kg^{-1} with arithmetic mean of 33.67 µg.kg^{-1}, NP$_2$ went from 1.68 to 24.24 µg.kg^{-1} with arithmetic mean of 11.10 µg.kg^{-1}, and NP$_3$ was measured at the concentrations of 9.3 to 55.89 µg.kg^{-1} with arithmetic mean of 23.88 µg.kg^{-1}, respectively. Subsequently, 4-n-OP and 4-tert-OP were only detected at station P14 of 1.77 µg.kg^{-1} and 2.89 µg.kg^{-1}, while five others stations were not detected.

Table 5.2. The distribution of APs proportions (%) throughout the stations

	Cortiou stations					
Stations	**Distance (m)**	**NP1**	**NP2**	**NP3**	**4-n-OP**	**4-t-OP**
P1	80	**53.07**	9.06	36.76	1.09	0
P4	230	19.86	9.7	68.6	1.82	0
P5	300	26.5	16.11	**57.37**	0	0
P12	380	13.24	13.83	**72.92**	0	0
P10	510	29.41	15.74	54.84	0	0
P11	570	**32.05**	13.26	53.88	0.79	0
P7	610	25.76	14.53	**59.7**	0	0
P8	680	28.81	15.24	55.93	0	0
Average		**28.59**	13.43	**57.50**	1.23	0
Stadeva		11.56	2.68	10.81	0.70	0
Beyond of Cortiou stations						
Stations	**Distance (km)**	**NP1**	**NP2**	**NP3**	**4-n-OP**	**4-t-OP**
P01	5.11	33.98	18.39	**47.56**	0	0
P02	4.89	30.81	25.01	**44.17**	0	0
P03	3.99	**54.4**	6.97	38.62	0	0
P04	2.9	77.7	8.3	13.96	0	0
P05	1.05	**56.91**	16.34	26.74	0	0
P14	3.67	34.52	18.71	43.15	1.36	2.23
Average		**48.05**	15.62	**35.7**	0	0
Stadeva		18.31	6.85	12.88	0	0

APs = Alkylphenols, NP = Nonylphenols, OP = Octylphenol

5.3.1.2. The distributions of APs proportions throughout the plume of Cortiou

The proportions of APs compositions were summarized in Table 5.2 and Figure 5.4 for Cortiou creek stations presented NP_1 of 13.24 to 53.07% with arithmetic mean of 28.59%, NP_2 of 9.06 to 16.11% with arithmetic mean of 13.43% and NP_3 of 36.76 to 72.92% with arithmetic mean of 57.50%. Further, 4-n-OP was observed as the lack proportion of 0.79 to 1.82% with arithmetic mean of 1,23%. These findings suggests that Cortiou stations was predominated by NP_3 isomers than others APs within surface sediments except station P1. On the other hand, the stations situated at outside of Cortiou consits of NP_1 which was ranged between 30.81 to 77.7% with arithmetic mean of 48.05%, NP_2 went from 8.3 to 25.01% with arithmetic mean of 15.62% and NP_3 was presented 13.96 to 47.56% with arithmetic mean of 35.7%. In the meantime 4-n-OP and 4-tert-OP were observed of 1.36% and 2.23%, repectively. Thus, it can be concluded that the stations adjacent to emissary point of WWTPs predominated by NP_1 with the proportions of 48.05%, NP_3 of 35.7% and NP_2 of 15.62% respectively. However, the Cortiou creek station provided the higher proportions of those compound compared to the out side of Cortiou which leads us to the fact that this site was strongly influenced by the direct input of WWTPs emissary point along with some local processes. The higher abundant of NP_1 and NP_3 was totally due to their similar fragmentation pattern than NP_2. This is the responsible of high occurrence of these chemicals in the environment (Moeder *et al* 2006).

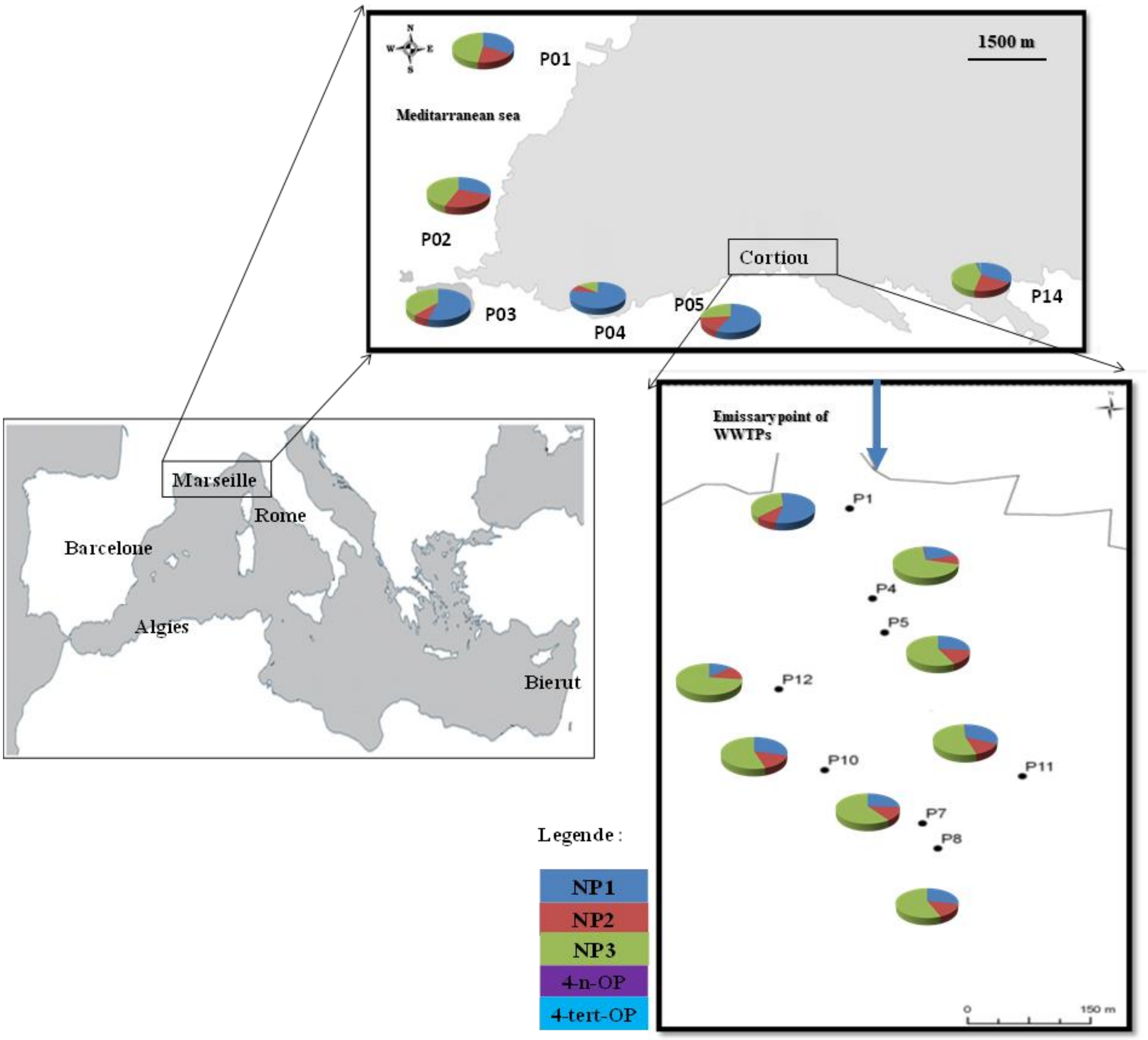


Figure 5.4. The distribution of APs proportions (%) throughout the stations

Table 5.3. The correlation matrices among NP mixtures, OP, total APs and TOC at Cortiou stations.

	NP1	**NP2**	**NP3**	**Tot NP**	**Tot OP**	**Tot APs**	**TOC (%)**
NP1	1						
NP2	0.61	1					
NP3	0.55	**0.93**	1				
Tot NP	0.80	**0.93**	0.94	1			
Tot OP	-0.61	-0.87	0.14	-0.99	1		
Tot APs	0.80	0.93	0.94	0.99	-0.99	1	
TOC (%)	-0.19	-0.02	-0.04	-0.09	0.96	-0.1	1

APs = Alkylphenols, NP = Nonylphenols, OP = Octylphenol, TOC = Total organic carbon

In order to determine how these chemicals link one another, we used coefficient correlations which are described in Table 5.3. It is statistically shows that NP1 has some positive correlations particularly with total NP and total APs with r^2 values of 0.80. This finding suggests that these compounds might have been derived from the same sources. Further, NP_1 has an anti-correlation with total APs and TOC which is unexpected. NP_2 has the strong positive correlations with NP_3, total NP and total APs with r^2 of 0.93. However, it has an anti-correlation with total OP and TOC distributions within surface sediments of Cortiou. NP_3 has the similar correlation as others NP isomers. Total NP has an anti-correlation with total OP in this study site which attributed that might be these substances derived from the different sources. None of APs has a positive correlation with TOC except total OP. This suggest that the sorption of APs within sirface sediments in this marine environment might be influenced by other factors.

Concerning two study site, Cortiou stations and outsisde of Cortiou, the coefficient correlation provided a statistically significant with r^2 >70% except their relation to total OP. It is clearly explained that these chemicals were derived from the same sources either directly from emissary point of WWTPs or direct input from others activities such as shipping traffic and domestic discharge.

Table 5.4. The correlation matrices among NP mixtures, tot NP, tot OP, total APs at all stations.

	NP1	**NP2**	**NP3**	**Tot NP**	**Tot OP**	**Tot APs**
NP1	1					
NP2	**0.72**	1				
NP3	**0.70**	**0.93**	1			
Tot NP	**0.79**	**0.94**	**0.96**	1		
Tot OP	-0.70	-0.59	-0.61	-0.98	1	
Tot APs	**0.76**	**0.92**	**0.98**	**0.95**	-0.27	1

APs = Alkylphenols, NP = Nonylphenols, OP = Octylphenol, TOC = Total organic carbon

We may conclud that the total concentrations of APs in Cortiou stations were ranged between 79.53 to 377.32 µg.kg^{-1} with arithmetic mean of 209.65 µg.kg^{-1}. These level of concentrations accompanied by TOC that was ranged between 0.8 to 8.8% with arithmetic of 3,3%. Those chemicals presente in various proportions that was predominated by NP_3 at the stations situated at the centre to the farthest stations of the plume. The outside of Cortiou stations provided the concentrations ranges 24,08 to 129.50 µg.kg^{-1} with arithmetic mean of 69.44 µg.kg^{-1}. It was observed that NP_1 appeared to be the prominent isomers in this area. There were the strong positive correlation among APs and NP isomers, however, there were not any correlation between APs presence in this area with total organic carbon (TOC) which is unexpected.

5.3.1.3. Comparison of APs levels within surficial sediments of Cortiou stations with other areas in the world.

We compared our results with several previous works that was globally carried out within the difference environmental matrices (marine, lacustrine and river sediments) as summarized in Figure 5.5 below. This comparison was determined only for NP mixture as the most abundant APs found within environment. As we pointed out earlier that the average concentrations of NP observed in Cortiou creek littoral area was 209.65 µg.kg^{-1}. These findings are largely lower than those investigated by Kurihara *et al* (2007) in Tokyo Bay of Japans (20700 µg.kg^{-1}) at the littoral sediments as the discharge of WWTPs. Mortazavi *et al* (2012) reported of 2940 µg.kg^{-1} in the Anzali wetland

Iran as the area linked to wastewater without treatment. In the meantime, Lardy-Fontan recorded in the Rade of Marseille of 1740 µg.kg^{-1} in Panier and 820 µg.kg^{-1} in Chantier as the sources from industrial, shipping activities and linked to WWTPs. However, Salgueiro-Gonzalez *et al* (2015) found the similar results as we observed in our environment in the coastal sediments of Glacia, Spain of 297,54 µg.kg^{-1}. Pojana *et al* (2007) at Venice Lagoon, Italie reported the lowest concentrations of these compounds of 88.87 µg.kg^{-1} as the discharge of industrial, agricultural and urban activities. These findings suggested that the most elevated contaminants of NP in littoral sediments were found majority associated with WWTPs. Furthermore, river sediment was contaminated by the massive concentrations of NP in Irish Shannon Catchment of 118000 µg.kg^{-1} as the impact of WWTPs. They also found in leachate and sludge of 36000 and 22800 µg.kg^{-1}. Bennie *et al* (1997) recorded in high level of NP concentrations in St. Lawrence River in Canada of 1050 µg.kg^{-1} as the impact of wastewater. Meanwhile Lardy-Fontan found in Heauveaune River of 850 µg.kg^{-1} which was impacted by industrial, agricultural and WWTPs. The lower results of our work and those found by Robert-Peillard in water sampling comparing to Lardy-Fontan which was carried out at the same study site might be due to the fact that those compounds have been banned in cleaning house product in France since 2005. Meanwhile sampling time of Lardy-Fontan was in 2004 and 2006 which were these products being employed. Whereas, our sampling campaign was carried out in 2010 which was distinctly implied that NPEO and their metabolites were no longer discharged into the environment. Kumar *et al* (2008) reported the lowest concentrations of NP at South Channel of Savannah River in USA of 13.36 µg.kg^{-1} as the impact of industries, factory and domestic activities. These findings still suggested that high concentrations of NP consistently has the link with WWTPs discharges as observed in several study site in the world. These are contrarily with those found by Lardy-Fontan (2008) in the Rade of Marseille which was suggested that WWTPs as the minority contributions in this marine environment.

Concerning lacustrine sediments Bennie *et al* (2007) and Zhang *et al* (2008) reported the high concentrations of NP in Lake of the Moon in China and The Great Lake Basin of Canada of 8400 µg.kg^{-1} and 15370 µg.kg^{-1} which were derived from WWTPs. Meanwhile in Shiwa Lake of Korea recorded 617 µg.kg^{-1} which was impacted by industrial activities. Figure 3.3 described clearly that the occurrence of NP was more elevated in river sediments comparing to marine and lacustrine.

It can be concluded that although the highest concentrations of NPs was found related to WWTPs discharge, there were some high concentrations of these compounds were reported derived from industrial, urban, factory and other activities in the different types of sediments. Nevertheless, the lower concentrations of NP were consistently have no relation to WWTPs discharge. Most recent works suggests lower concentrations of these chemicals than the studies in the pass which implies that NP has been banned (in France, 2005) thus they are no longer being employed.

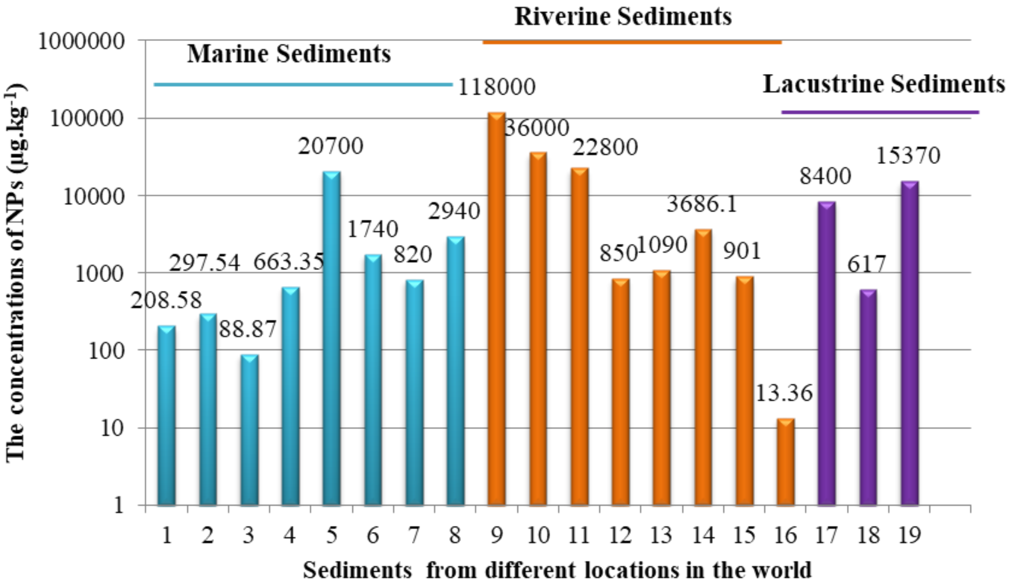


Figure 5.5. Sedimentary concentrations for different sites throughout the world

**y axis in logarithmic scale*

Legende : 1 Recent sudy, Cortiou Marseille (France), 2. Salgueiro-Gonzalez *et al* (2015) (Espagne) 3. Pojana *et al* (2007) (Italie), 4. Xu *et al* (2015) (Chine), 5. Kurihara *et al* (2007) (Japons), 6. Lardy-Fontan, France (2008) (France) 7. Lardy-Fontan, France (2008) (France), 8. Mortazavi *et al* (2012) (Iran), 9. Reid *et al* (2009) (Irlandia) 10. Reid *et al* (2009) (Irlandia), 11. Reid *et al* (2009) (Irlandia), 12. Lardy-Fontan *et al* (2008) (France), 13. Bennie *et al* (1997) (Canada) 14. Gong *et al* (2011) (China), 15. Llorca-Porcel *et al* (2009) (Espagne), 16. Kumar *et al* (2008) (USA), 17. Zhang *et al* (2008) (China), 18. Li *et al* (2004) (Korea), 19. Bennie *et al* (1997) (Canada), 20. Venkatesan and Halden (2013) (USA).

5.3.1.4. The deviation of the plume under the influence of hydrodynamic conditions

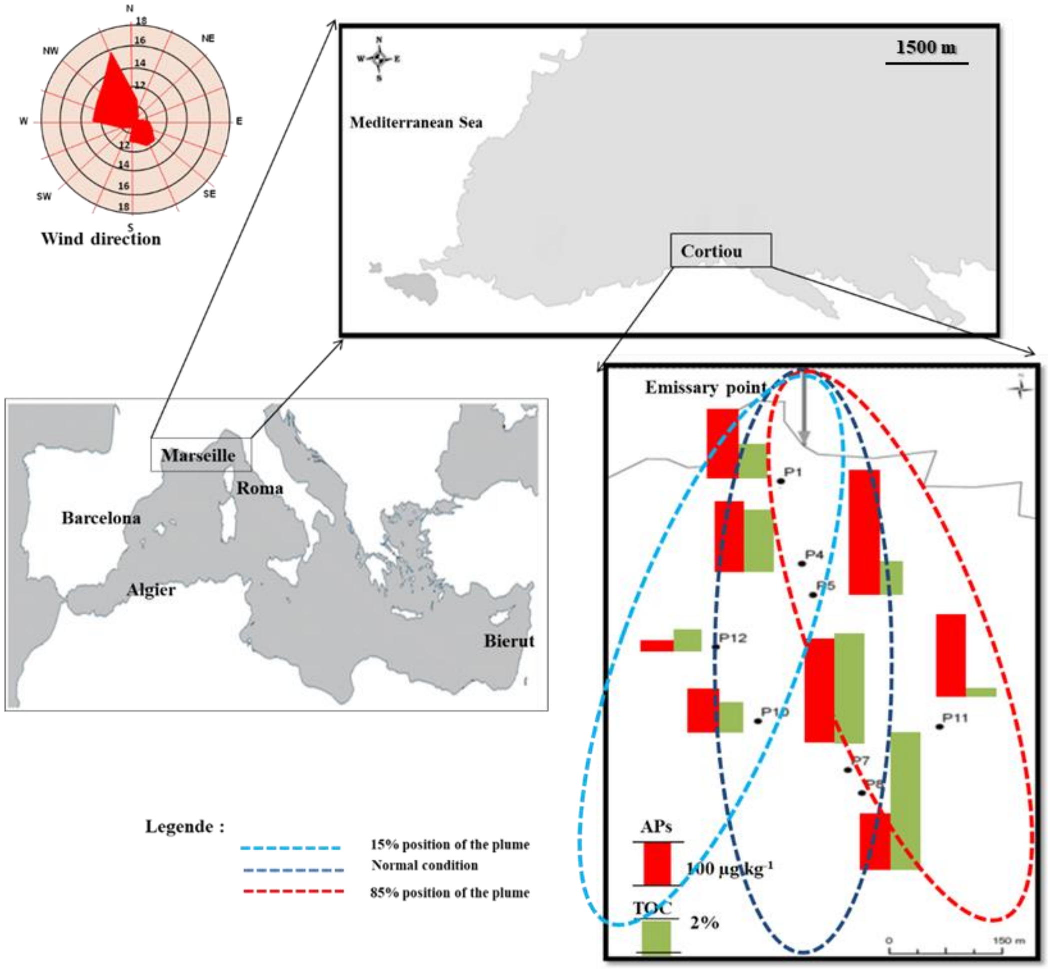


Figure 5.6. The deviation of the plume under influences of wind direction in Cortiou stations.

We observed that the concentrations of APs were significantly more elevated in the eastern side (P5 and P11) of the plume than those in the western side (P12 and P10). It can be seen in Figure 5.6 that the plume is deviated under the influence of the prevailing wind as shown in the wind-rose diagram. In the normal condition, the plume flows southward to the offshore, however, the plume deviates southeastward as the effect of the upwelling phenomenon due to the wind and the turbulence effects. This direction occurs to be 85% throughout the year. On the other hand 15% of the plume direction deviates to southwestward (Fraysse *et al* 2013). These processes might export these chemicals more concentrated at the eastern stations in this marine environment.

5.3.1.5. Physico-chemical parameters influencing APs distribution

The physic parameters that were measurable in this work related to the distribution of APs concentrations are summarized in Table 5.8 and Figure 5.9 including Al, Li, Pb and particle sizes (silt, clay and sand). **These parameters are believed to be the important factors to enhance the processes of coagulation and flocculation of organic contaminants within water column (Shon *et al* 2009; Zhu *et al* 2011; When *et al* 2015)**. The conservative elements (Al and Li) also adequately reflect the granulometric variability in the sediments in the study area (Soto-Jimenez and Paez-Ozuna, 2001). In order to determine the relations among those parameters with the spatial evolutions of APs throughout the plume, we statistically analysed the correlation coefficient as summarized in Table 5.5 and 5.6.

Table 5.5. The distribution of trace elements and particle sizes throughout the plume at Cortiou creek stations.

Stations	**Al (µg.g^{-1})**	**Li (µg.g^{-1})**	**Pb (µg.g^{-1})**	**Clay(%)**	**Silt(%)**	**Fine sand(%)**
P1	3445	5.87	60	15.50	31.25	31.43
P4	7993	11.75	90	19.92	37.61	22.76
P5	6680	11.72	120	36.01	55.33	2.07
P12	4111	7.73	250	24.17	60.69	3.03
P10	3172	4.58	230	12.82	50.99	14.7
P11	2939	5.23	100	22.11	63.17	4.15
P7	12485	21.22	170	26.12	56.05	4.36
P8	15008	24.91	180	27.9	64.85	0.39

Al = Aluminium, Li = Lithium, Pb = lead

Table 5.6. The correlation matrices among APs, NP isomers and physico-chemical parameters

	NP1	**NP2**	**NP3**	**Tot NP**	**Tot OP**	**Tot APs**	**TOC**	**Al**	**Li**	**Pb**	**Clays**	**Silts**	**Fine sands**
NP1	1												
NP2	0.61	1											
NP3	0.55	0.93	1										
Tot NP	0.80	0.93	0.94	1									
Tot OP	0.80	-0.87	0.14	-0.99	1								
Tot APs	0.80	0.93	0.94	0.99	-0.99	1							
TOC	-0.19	-0.02	-0.04	-0.09	0.96	-0.10	1						
Al	-0.21	0.10	0.13	0.01	0.96	0.00	0.96	1					
Li	-0.18	0.10	0.14	0.03	0.96	0.03	0.96	0.99	1				
Pb	**-0.78**	-0.36	-0.49	-0.64	-0.09	**-0.65**	0.18	0.10	0.13	1			
Clays	0.08	**0.66**	**0.59**	**0.48**	-0.18	0.47	0.33	0.49	0.54	0.01	1		
Silts	-0.43	0.13	-0.03	-0.16	-0.65	-0.17	0.31	0.30	0.35	0.57	0.53	1	
Fine sands	0.36	-0.32	-0.18	-0.01	0.55	0.00	-0.35	-0.39	-0.45	-0.53	-0.72	-0.96	1

TOC = Total organic carbon, NP = Nonylphenol, OP = Octylphenol, APs = Alkylphenols, Al = Aluminium, Li = Lithium, Pb = Lead.

The coefficient correlations among APs and the isomers of NP with trace elements and particle sizes described in Table 5.6. It is shown that NP isomers have the strong positive correlations among them and also with total OP and total APs. Concerning their relation with trace elements and particle sizes, NP_1 isomer did not show any correlations with Al, Li and Pb. However, NP_2, NP_3 and total NP provide slightly positive correlations to clays with r^2 values of 0.66, 0.59, 0.48. These findings suggested that there was significantly positive correlation between the adsorbabilities of these sedimentary organic contaminants to the fine particle sizes such as clay. On the other hand, trace elements did not play an important role to these organic matters settling which were unexpected (Lin and Chen 1997). This suggested that other factors were equal or larger importance that has determined the distribution of APs in this study site. Interestingly that Pb has an anti-correlation to NP$_1$ and Total APs which is converselywith the results suggested by Bojakowska *et al* (2013). This is probably suggested that a mix factors were stimulating the sorbtion of these substances in sediments.

5.3.2. The distribution of APs in soil at Cortiou creek stations.

The spatial evolutions of APs within surface soil samples in Cortiou creek were summarized in Table 5.7 A and 5.7 B and Figure 5.7. Those chemicals consisted of NP$_1$, NP$_2$, NP$_3$, 4-n-OP and 4-tert-OP which were distributed through six stations. We divided our study area into two zones, those exposed to the southeast wind and those protected by this aerodynamic factors at the eastern side. For those stations under affected by southeast wind, the concentrations of NP$_1$ was measured between 21.32 to 81.87 µg.kg^{-1} with arithmetic mean of 48.08 µg.kg^{-1}, NP$_2$ was ranged from 14.41 to 29.47 µg.kg^{-1} with arithmetic mean of 19.39 µg.kg^{-1} and NP$_3$ was measurable of 142.07 to 461.12 µg.kg^{-1} with arithmetic mean of 339.13 µg.kg^{-1}, respectively. Subsequently, 4-n-OP concentrations provided 20.97 to 80.45 µg.kg^{-1} with arithmetic mean of 50.71 µg.kg^{-1}, whereas 4-tert-OP was detected at a single station (S3) of 24.1 µg.kg^{-1}. These values were accompanied by total organic acrbon (TOC %) which were ranged between 7.12 to 19.99% with arithmetic mean of 13.16%. Meanwhile, the protected stations provided NP$_1$ concentrations of 6.2 to 12 µg.kg^{-1} with arithmetic mean of 9.1 µg.kg^{-1}, NP$_2$ went from 3.13 to 8.56 µg.kg^{-1} with arithmetic mean of 5.84 µg.kg^{-1}, and NP$_3$ was ranged between 28.83 to 54.00 µg.kg^{-1} with arithmetic mean of 41.41 µg.kg^{-1}, respectively. 4-n-OP was only observed at station S5 of 44.65 µg.kg^{-1} while 4-tert-OP was not detected in this site. At the same time, TOCs were measurable between 8.28 to 9.84% with arithmetic mean of 8.88%.

Table 5.7. The distribution of APs and TOC in soil near Cortiou creek.

	Coordinate positions								
(A)	Longitude	Latitude	**Stations exposed to southeast wind**						
Stations			NP1	NP2	NP3	4-n-OP	4-t-OP	∑APs	TOC (%)
S1	43°1'51.46"	5°24'8.66"	59.06	29.47	396.8	80.45	nd	565.78	11.55
S2	43°12'53.97"	5°24'3.67"	30.09	18.86	356.55	nd	nd	405.5	**19.99**
S3	43°12'56.63"	5°23'59.49"	81.87	14.81	**461.12**	20.97	24.1	**602.47**	**13.96**
S4	43°13'1.92"	5°23'55.67"	21.32	14.83	142.07	nd	nd	178.22	7.12
Total	43°1'51.46"	5°24'8.66"	192.34	77.97	**1356.34**	101.42	24.1	**1751.97**	52.62
Average			48.08	19.49	339.13	50.71	0	437.99	13.16
Stadeva			27.70	6.92	138.26	38.04	0	193.15	5.37
(B)			**Stations protected to southeast wind**						
S5	43°12'55.13"	5°24'9.18"	12	8.56	54	44.65	nd	119.21	9.48
S6	43°12'53.97"	5°24'12.64"	6.2	3.13	28.83	nd	nd	38.15	8.28
Total			18.2	11.69	82.83	44.65	0	157.36	17.76
Average			9.1	5.84	41.41	0	0	78.68	8.88
Stadeva			4.10	3.84	17.80	0	0	57.32	0.85

These concentration values (Table 5.7 A and B) were obtained by the method precision assessed by replicate injection of standard solution (n = 6) expressed as the ralative standard deviation (RSD). RSD on the calculated concentrations of the replicates was less than 15%.

APs = Alkylphenols, NP = Nonylphenols, OP = Octylphenol, TOC = Total organic carbon, nd = not detected.

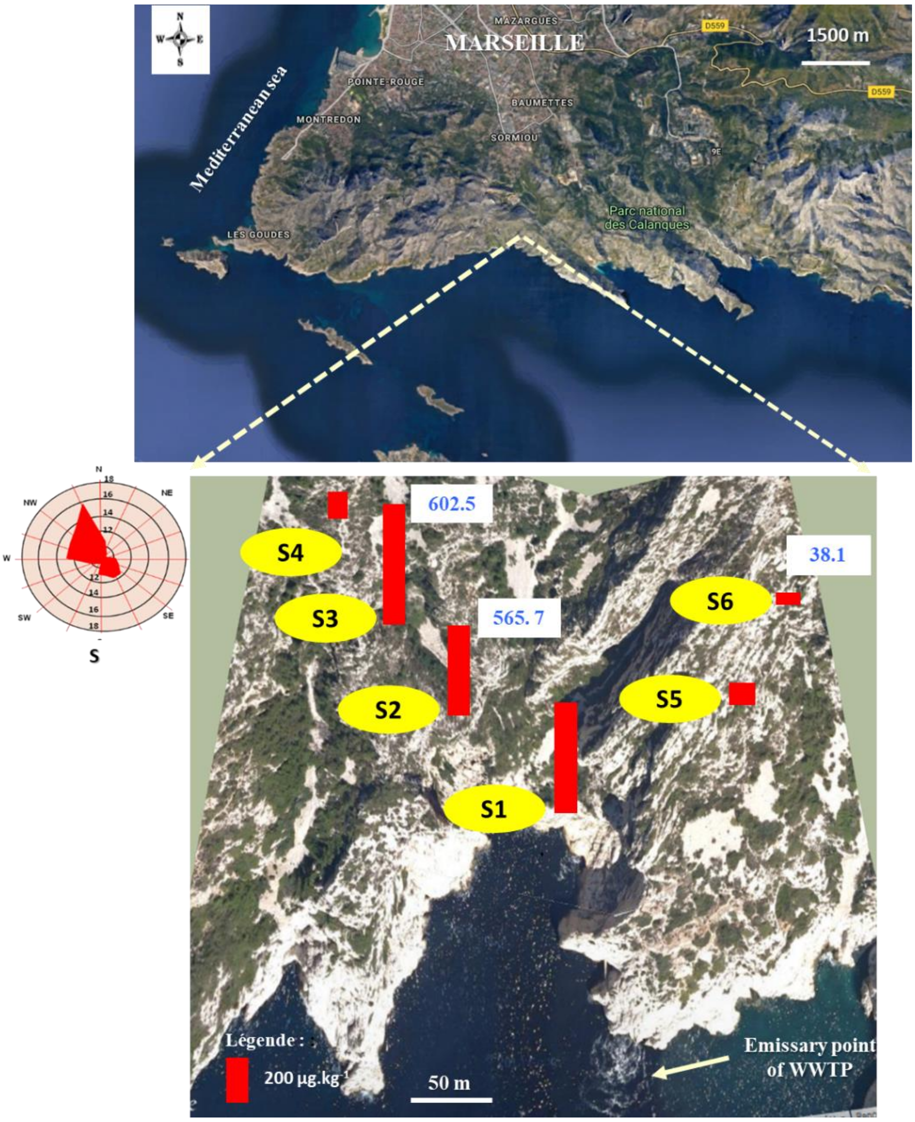


Figure 5.7. The distributions of total APs (ΣAP) in soil as a function of the distance from emissary point of WWTPs.

5.3.2.1. The distribution of APs proportions in soil at Cortiou creek stations

The distribution of APs proportions within soil samples was described in Table 5.8. Concerning the exposed stations, it can be seen that NP$_1$ presented in 7.42 to 13.59% with arithmetic mean of 10.85%, NP$_2$ went from 2.39 to 8.32% with arithmetic mean of 5.14%, and NP$_3$ was ranged between 70.13 to 87.93% with arithmetic mean of 78.58%. Whereas 4-n-OP provided 3.48 to 14.22% with arithmetic mean of 8.85%. These findings suggested that the concentrations of APs were more important at the stations exposed to the southeastern wind. This aerodynamic factor might have driven those substances as the particularly impact of WWTP's emissary point via the possibility transfer of marine aerosols then deposited in soil surface. Meanwhile, the eastern side (S5 and S6) presented the concentration of APs throughout stations varied between 0.10 to 16.25 % with arithmetic mean of 8.18 % for NP$_1$, 7.18 to 8.20 % with arithmetic mean of 7.69 for NP$_2$ and 45.30 to 75.57% with arithmetic mean of 60.44% for NP$_3$, respectively. Meanwhile, 4-n-OP was presented 37.45% and 4-

tert-OP was not detected. It is clearly shown that the important compund is NP_3 which presented the highest proportion at the entire of the difference zones, followed by NP_1 and NP_2 as the least one. While 4-n-OP and 4-tert-OP were observed in poor proportions. This suggested that NP_3 was the prominent within surficial soil in two zones either in Cortiou stations or outside of Cortiou.

The correlations among APs with NP isomers and TOC were summarized in Table 5.9 below. It is distinctly shown that these compounds have a strong positive correlations one another with r^2 values ranged between 0.60 to 0.99 except NP_1, NP_3 and total NP with total OP. These findings suggest that the NP isomers and total APs might have been derived from the same sources except OP. They also have a good positive correlations with TOC except NP_1 and NP_2 which have slightly positive correlations with r^2 values of 0.39 and 0.40. These explain that the sorption of these contaminants within surface soil was controlled by organic carbons in this marine environment.

Table 5.8. The distribution of APs proportions (%) in soil near Cortiou creek.

(A)	**Distance (m)**	**Stations exposed to southeast wind**				
Stations		**NP1**	**NP2**	**NP3**	**4-n-OP**	**4-t-OP**
S1	147	10.44	5.21	70.13	14.22	nd
S2	277	7.42	4.65	**87.93**	nd	nd
S3	405	13.59	2.39	**76.54**	3.48	3.13
S4	589	11.96	8.32	79.72	nd	nd
Average		10.85	5.14	**78.58**	8.85	0
(B)		**Stations protected to southeast wind**				
S5	235	12	8.56	54	44.65	nd
S6	395	6.2	3.13	**28.83**	nd	nd
Average		9.1	5.84	41.41	0	0

APs = Alkylphenols, NP = Nonylphenols, OP = Octylphenol, nd = not detected.

Table 5.9. The correlation matrix between APs, NP isomers and TOC in soil of Cortiou stations.

	NP1	**NP2**	**NP3**	**Tot NP**	**Tot OP**	**Tot APs**	**TOC (%)**
NP1	1						
NP2	**0.60**	1					
NP3	**0.91**	**0.75**	1				
Tot NP	**0.93**	**0.75**	0.99	1			
Tot OP	0.21	**0.97**	0.37	0.38	1		
Tot APs	**0.95**	**0.78**	**0.98**	**0.99**	0.44	1	
TOC (%)	0.39	0.40	0.68	0.64	-0.03	0.60	1

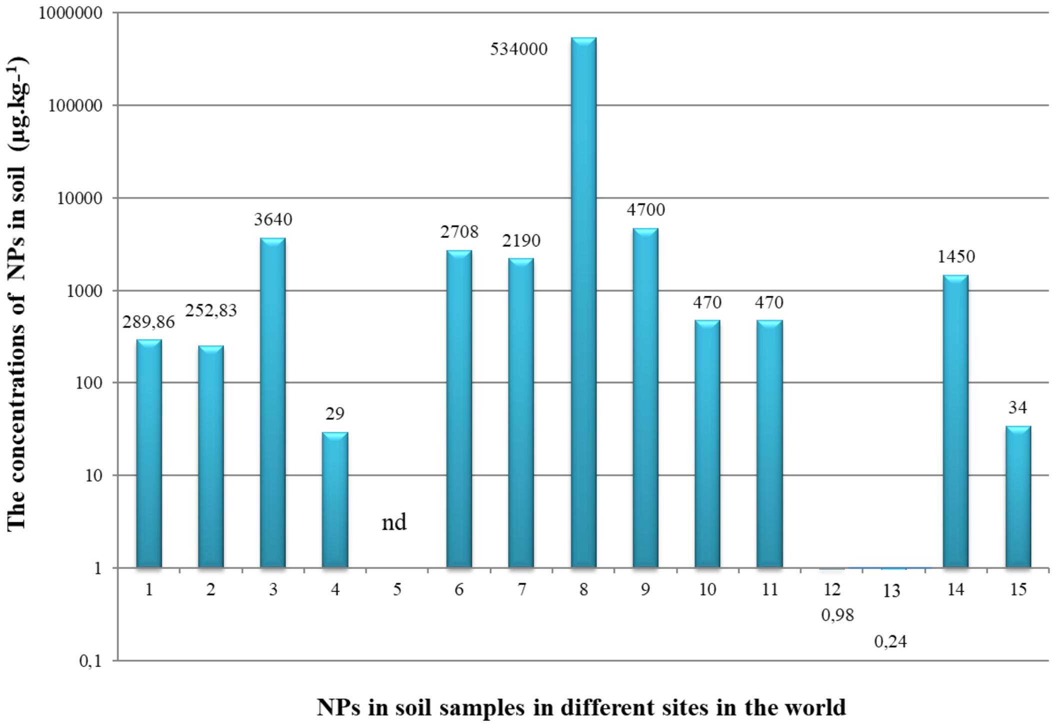
Partial conclusion

Total APs concentrations for the stations exposed to the southeast wind within surface soil at Cortiou stations were measured between 178.22 to 602.47 µg.kg^{-1} with arithmetic mean of 437.99 µg.kg^{-1}. Another side stations provided 38.15 to 119.21 µg.kg^{-1} with arithmetic mean of 78.68 µg.kg^{-1}. It is suggested that the stations under influence of southeast wind contributed the higher concentrations of APs within surface soil than the protected ones. Meanwhile NP_3 was appeared to be the prominent isomer throughout the stations. The emissary point of WWTPs presumably plays an important role in contributing the residues of APs both within marine sediments and soil samples.

5.3.2.2. Comparison with other sites

As we observed in our work that the average of total NP concentrations at Cortiou was 289.86 µg.kg^{-1}. Comparing to the values observed in Figure 5.9, our results are largely lower than those reported by Venkatesan and Halden 2013 which was massively found of 534000 µg.kg^{-1} within sludge and amended soils. Marcomini *et al* 1989 (within the sludge) and Hawrelak et al 1999 (within industrial discharges) also found in a huge amount of NP concentrations of 4750 µg.kg^{-1} and 3640 µg.kg^{-1}. Furthermore, Gibson *et al* (2005) and Ojeda *et al* (2013) and found largely NPs concentrations within amended soils, sludge and impacted by microbial activities of 2708 µg.kg^{-1} and 2190 µg.kg^{-1}. Nevertheless, several works found NPs in low concentrations such as Andreu et al 2007 reported 252.83 µg.kg^{-1} within WWTPs discharge, while Stanford and Weinberg (2007) found only 29 µg.kg^{-1} in the irrigation zone. Vikelosoe *et al* 2002 found these compounds in natural soil of 0.98 to 470 µg.kg^{-1} while in fertilize soil, they found 0.24 µg.kg^{-1}. These chemicals were not detected within natural soil that was observed by Gibson *et al* 2005 in UK.

It is clearly suggested that the majority of NPs contaminants were found within soil samples link to WWTPs discharge and industrial activities. Nevertheless, they also found within natural soil which suggests that these chemicals could be disseminated and transported from the different matrices in the environment.



**y axis in logarithmic scale*

Legende :

1. Recent work, 2. Andreu et al 2007 (Europe Mediterranean), 3. Hawrelak et al 1999 (Canada), 4. Stanford and Weinberg 2007 (USA), 5. Gibson et al 2005 (Royaume-uni), 6. Gibson et al 2005 (UK), 7. Ojeda et al 2013 (Espagne), 8. Venkatesan and Halden 2013 (USA), 9. Marcomini et al 1989 (Italy), 10 - 15. Vikelosoe et al 2002 (Denmark)

Figure 5.8. The quantification of NPs concentrations within soil samples in different sites troughout the world.

Since the prominent compounds found in soil samples are NP as we presented in the case of sediments, we displayed the three isomer of NP in order to observe weather or not they have the similarity of distribution in term of their compositions and spatial distribution. It is suggested that the spatial evolution of NP was largely deposited at the western side (S1 to S4) of the valley where is under the influence of south east wind than another side (S5 and S6) where is more protected. Meanwhile the compositions of APs were still dominated by NP_3 as occurred in the deposition of these chemicals in sediments of Cortiou.

5.3.2.3. Determinations of the similarity sources of APs in soil and sediment samples

In order to obtain the values indicated whether or not APs within soils and sediments were derived from the same sources, we employed the indices of NP isomers to APs as summarized in Table 5.10 (A) and (B). These ratio shows that NP_1 in sediments was ranged between 0.13 to 0.53 with arithmetic mean of 0.28, NP_2 went from 0,09 to 0,16 with arithmetic mean of 0.13, and NP_3 provided 0,37 to 0.73 with arithmetic of 0,57. Meanwhile, this ratio in soil samples (5.10 (B) contributed 0.07 to 0.16 with arithmetic mean of 0.11, NP_2 was ranged between 0.02 to 0,08 with arithmetic mean of 0,06. In the meantime, NP_3 was found between 0.45 and 0.88 with arithmetic mean of 0.72. These results show the ratios were slightly similar one another which suggested that those chemicals might have been derived from the same sources to settle at the difference matrices either marine sediments or soil in the vicinity of coastal area.

Table 5.10. Ratio of NP/APs in soil and sediment samples in Cortiou creek area.

(A)	**Sediments**		
Stations	**NP1/AP**	**NP2/AP**	**NP3/AP**
P1	0.53	0.09	0.37
P4	0.2	0.1	0.69
P5	0.27	0.16	0.57
P12	0.13	0.14	0.73
P10	0.29	0.16	0.55
P11	0.32	0.13	0.54
P7	0.26	0.15	0.6
P8	0.29	0.15	0.56
Average	**0.28**	**0.13**	**0.57**
Stadeva	0.12	0.03	0.11
(B)	**Soils**		
S1	0.1	0.05	0.7
S2	0.07	0.05	0.88
S3	0.14	0.02	0.77
S4	0.12	0.08	0.8
S5	0.1	0.07	0.45
S6	0.16	0.08	0.76
Average	**0.11**	**0.05**	**0.72**
Stadeva	0.03	0.02	0.15

In order to determine the different concentrations of APs within surface soil in the two different zones, we divided our study site to be two areas. The first one situated at the western side wherein the soil is under influence of southeast wind and another side where is protected by this aerodynamic factor. The concentrations of total APs within surface soil distributed unevenly at two different zones in which the western side was influenced by southeast wind while another side was rather protected. For those stations exposed to the prevailing wind from southeast, the total APs concentrations were ranged 178.22 to 602.47 µg.kg^{-1} with arithmetic mean of 437.99 µg.kg^{-1}. Meanwhile, the concentration levels of total APs at another side went from 38.15 to 119.21 µg.kg^{-1} with arithmetic mean of 76.68 µg.kg^{-1}. It is clearly shown that the most elevated concentrations was occurred at the stations impacted by south-east wind, whereas the lowest concentrations were taken place at the protected stations.

The regression coefficient correlation showed that TOC and particle sizes shows a slightly positive correlation with r^2 value of 0.41 and 0.20 respectively to the distribution of APs concentrations within surface soil of Cortiou. These results attributed to the fact that TOC and particle sizes provided a slightly impact to the sorption of APs and NP_3 isomers within soil samples at Cortiou creek.

Table 5.11. The distribution of APs, TOC and particle sizes in soil near the emissary point of WWTPs near Cortiou creek.

(A)	**Stations exposed to southeast wind**									
Stations	**NP1**	**NP2**	**NP3**	**4-n-OP**	**4-t-OP**	**∑APs**	**TOC (%)**	**Clay(%)**	**Silt(%)**	**Fine sand(%)**
S1	59.06	29.47	396.8	80.45	nd	565.78	11.55	10.1	42.46	20.82
S2	30.09	18.86	356.55	nd	nd	405.5	**19.99**	8.97	42.03	19.9
S3	81.87	14.81	**461.12**	20.97	24.1	**602.47**	**13.96**	**26.12**	**56.05**	4.36
S4	21.32	14.83	142.07	nd	nd	178.22	7.12	10.19	**47.61**	15.2
Total	192.34	77.97	**1356.34**	101.42	24.1	**1751.97**	52.62	55.79	188.15	60.28
Average	48.08	19.49	339.13	50.71	0	437.99	13.16	13.94	47.03	15.07
Stadeva	27.70	6.92	138.26	38.04	0	193.15	5.37	8.14	6.52	7.55
(B)	**Stations protected to southeast wind**									
S5	12	8.56	54	44.65	nd	119.21	9.48	21.45	**57.38**	5.7
S6	6.2	3.13	28.83	nd	nd	38.15	8.28	24.05	**54.2**	4.77
Total	18.2	11.69	82.83	44.65	0	157.36	17.76	45.5	111.58	10.47
Average	9.1	5.84	41.41	0	0	78.68	8.88	22.75	55.79	5.23
Stadeva	4.10	3.84	17.80	0	0	57.32	0.85	1.84	2.25	0.66

APs = Alkylphenols, NP = Nonylphenols, OP = Octylphenol, TOC = Total organic carbon, nd = not detected.

In order to determine the correlation among these APs with particle sizes, we statistically used the regression coefficient correlation. It is distinctly shown that silt and clay did not have any positive correlations to the presence of APs in surface soil which is unexpected. However, total OP and total APs have some strong positive correlations with fine sand with r^2 of 0,82 for NP_2 and 0,99 for total OP. In the meantime, total NP isomers and total APs have a slightly positive correlation with TOC in this area. It means that TOC has play an important role regarding the sorption processes of organic contaminants.

We can conclude that the APs which settled in the area exposed to the prevailing wind from the south east of the sea, those composition were similar to the APs deposited in marine sediments (Figure 5.9). It was found that NP_3 predominated in sediments at Cortiou stations and soils near Cortiou as well. The constantly of its contribution in both different samples (sediments and soils) indicates that this compound is a possible tracer common area of contamination. The intensity of AP and NP_3 settling at the stations exposed to the wind influences were slightly controlled by TOC but not particle fraction. Thus, we may orient to the compound deposited in soils related to the particular topography of the site where the relief preferential corridors of circulation and the zone where aerodynamic energy was lost.

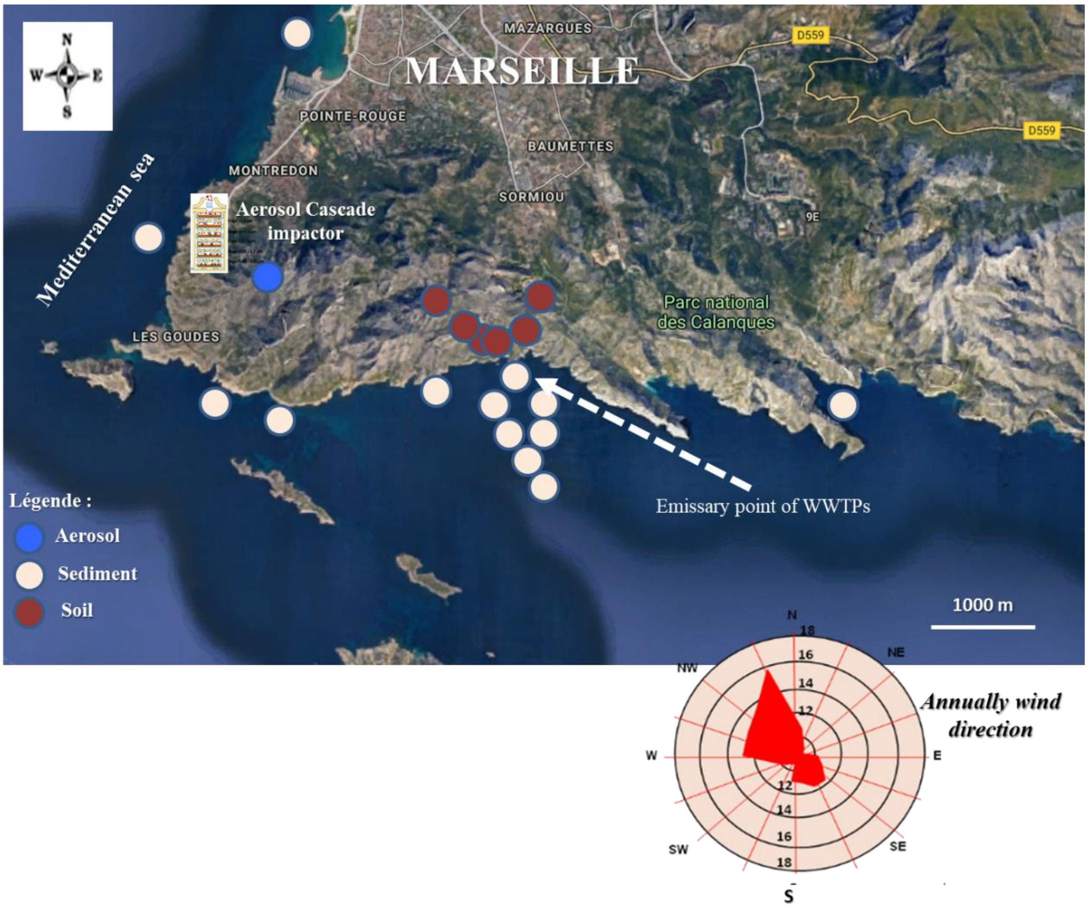


Figure 5.9. The general distribution of APs concentrations at the difference matrices under the influence of aerodynamic.

5.3.3. Distribution of APs concentrations in aerosols in the vicinity of Cortiou

With the help of anemometric condition we used the cascade impactor positioning in order to observe the aerosols samples which was set up at Col de Moute (approximately 4,5 km west of Cortiou at the geographic position of 43°13’21.96” N and 5°21’4.55” E. The samples measured were varied in 5 different sizes of filters of 0.49 – 0.96 µm. 0.92 – 1.5 µm, 1.5 – 3 µm, 3 – 7.2 µm, > 0.72 µm. According to the information from environmental matrices (sediments and soils) have been indicating what was taking place in the vicinity of WWTP’s emissary point, the data of APs in aerosols allow us to visualize the footprint of APs were transported farther from the emission zones.

The concentrations of three NP isomers which were obtained from 5 filter sizes are summarized in Figure 5.10. Total concentrations of NPs in aerosols at Col de Moute ranged between 2.94 and 16.2 $ng.m^{-3}$ which were consisted of NP_1 ranged from 1 to 3.45 $ng.m^{-3}$ with arithmetic mean of 2.3 $ng.m^{-3}$, NP_2 varied between 0.61 to 1.16 $ng.m^{-3}$ with arithmetic mean of 0,81$ng.m^{-3}$ and NP_3 went from 1,32 to 12.2 ng.m^{-3} with arithmetic mean of 8,46 ng.m^{-3}. On the other hand, 4-n-OP and 4-tert-OP was not detected.

Furthermore, we observed that the three major classes correspond to particles ranging from 0.92 to 7.2 microns. The two majority classes reached about 16 ng.m^{-3}. 88% of AP in these 3 classes (Figure 5.11). The values found are in the average of the results encountered in several previous works.

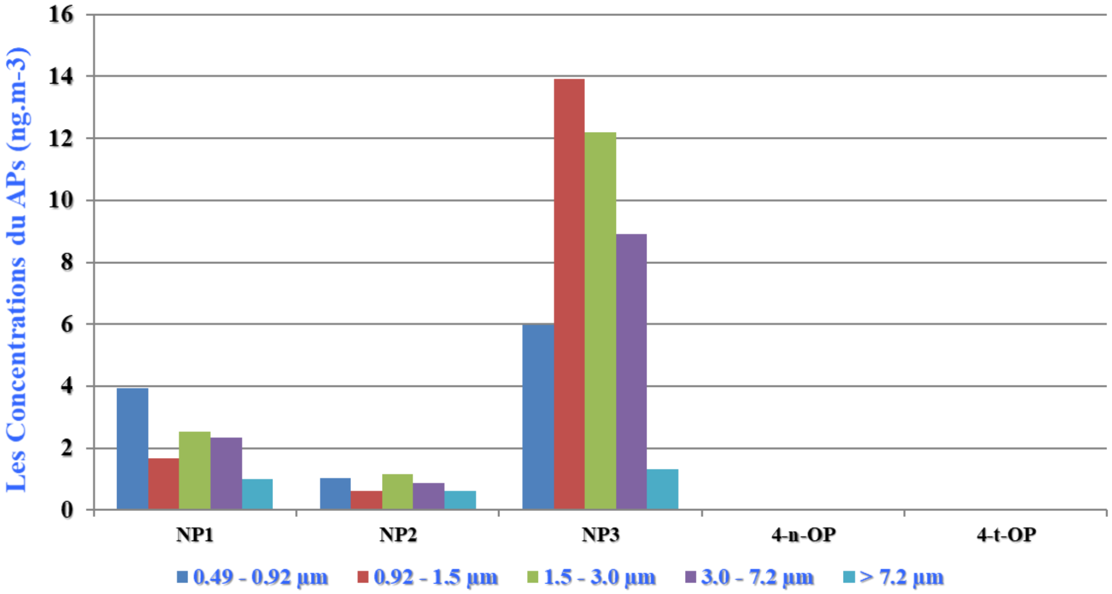


Figure 5.10. The distribution of APs concentrations in aerosols (ng.m^{-3}) at Cole de Moute ±5 km from emissary point of WWTPs.

These results were largely lower than those found by Wilson *et al* (2001) in USA (100 ng.m^{-3}) in urban area; Ying *et al* (2006) in USA (690 ng.m^{-3}) in indoor air; Saito *et al* (2014) in Japans (90 ng.m^{-3}). Nevertheless, these findings were higher than those reported by Berkner *et al* (2004) in Germany (1.7 – 117 pg.m^{-3}) in the mountains area; Moreau-Guigon and Chevreuil (2014) in France (0,9 – 2 ng.m^{-3}) in urban centre. Furthermore, our results were more and less similar to the results recorded by Van Ry *et al* (2000) in USA (7 ng.m^{-3}) in metropolis area; Salapasidou *et al* 2011 in Greece (4.96 ng.m^{-3}) in urban and industrials area; Saito *et al* (2014) in Japans (6 ng.m^{-3}) in urban area (Table 5.12). The magnitude of the concentrations suggested that the compounds are more elevated in indoor than outdoor ones. It is important to mention that there was some enrichment of NP at the area influenced by urban activities and industrial area than the natural ones which is plausible.

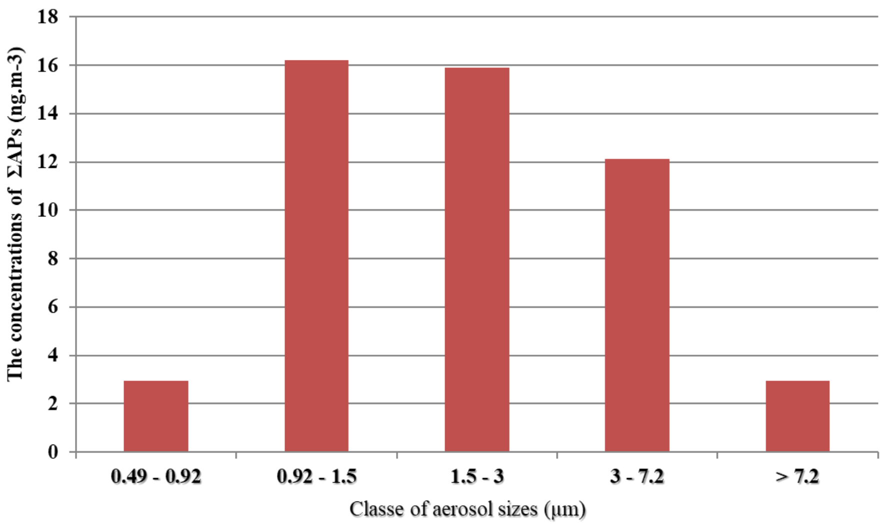


Figure 5.11. The distribution of ∑APs as a function of the aerosol particle sizes

Table 5.12. The comparison of NP occurrence in aerosols samples throughout the world

No	Sources	Concentrations	References	Geographic Location
		NP (ng.m^{-3})		
1	Aerosol from urban center	0.8	Moreau-Guigon et Chevreuil 2014	France
2	Nursery room	70	Moreau-Guigon et Chevreuil 2014	France
3	Exterior Aerosols	90	Saito *et al* 2004	Japans
4	Interior Aerosols	690	Ying *et al* 2006	USA
5	Aerosols impacted by urban traffic	5.12	Salapasidou *et al* 2011	Greece
6	Aerosols impacted by urban industrial	4.96	Salapasidou *et al* 2011	Greece
7	Aerosol of metropolis neighborhood	3.25	Van Ry *et al* 2000	USA
8	Marine Aerosols	0.005 – 0.017	Xie *et al* 2006	Norway
9	Urban Aerosols	6	Saito *et al* 2004	Japans
10	Urban Aerosols	7	Van Ry *et al* 2000	USA
11	Urban Aerosols	100	Wilson *et al* 2001	USA
12	Aerosols of the mountain	0.001 – 0.1	Berkner *et al* 2004	Germany
13	Marine aerosols impacted by urban activities	0.1 – 51	Dachs *et al* 1999	USA

NP = Nonylphenols, USA = United State of America

The distributions of NPs isomers concentrations in aerosols were predominated by NP_3 varying between 1.32 to 13.91 $ng.m^{-3}$ with arithmetic mean of 8.46 $ng.m^{-3}$. The most elevate concentrations of NP_3 was occurred in particle size of 0.92 to 7.2 µm which are well-categorized as primary marine aerosols (PMA) as suggested by (Nilsson *et al* 2001; Geever *et al* 2005; Clarke *et al* 2006). These particle modes were majority derived from sea salt (Grass and Ayers, 1983). On the other hand, we also found the particle size with $r < 0.25$ µm as fine mode particle which is predominantly of non-sea salt sulphate (nss-sulphate).

5.4. The evaluation of APs origins in the different matrices of Cortiou stations

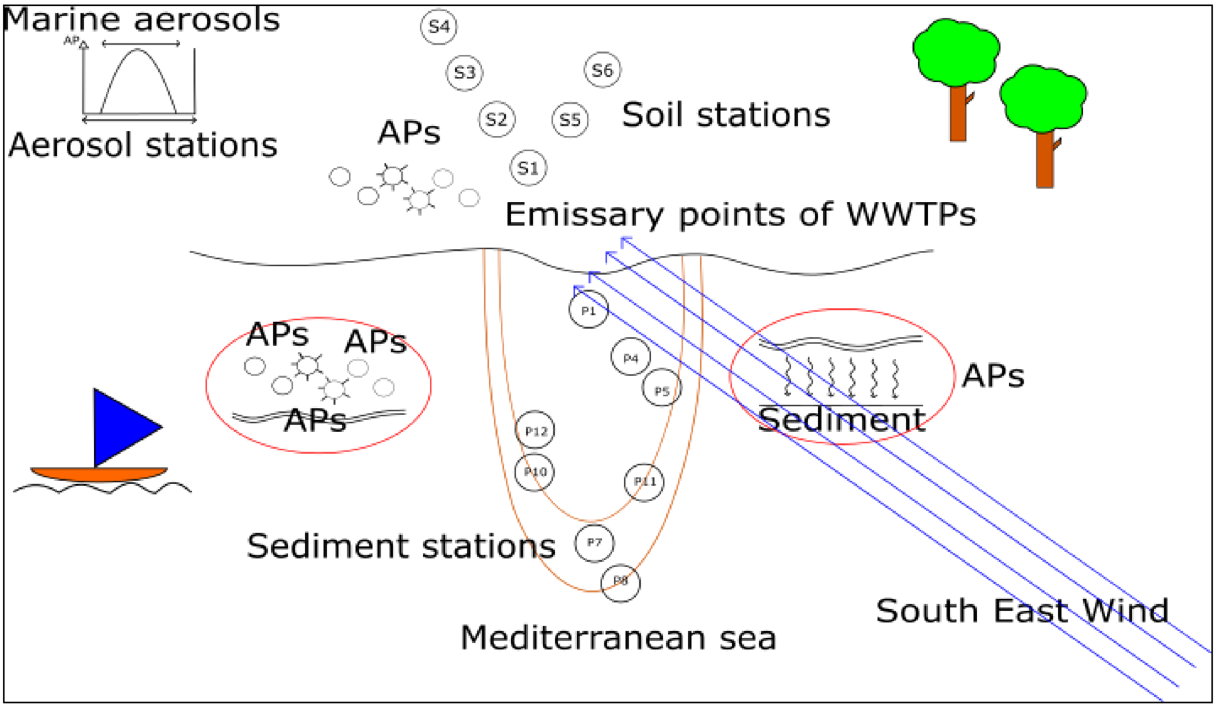
In order to investigate whether or not these compounds from three different matrices derived from the similar sources, we quantify the indices between NP/AP. The indices provided the similar values for these matrices (sediment, soil and aerosol) as summarized in Table 5.13 that can be seen that the ratios of NP_1 in sediments ranged between 0.13 to 0.53 with arithmetic mean of 0.29, while in soil samples were observed of 0.07 to 0.16 with arithmetic mean of 0.12. The aerosols matric provided 0.10 to 0.36 with arithmetic mean of 0.23, respectively. For NP_2 isomer contribution in sediment ranged between 0,09 to 0,16 with arithmetic mean of 0.13, while soil samples provided 0.02 to 0.08 with arithmetic mean of 0,08 and aerosols contributed as 0.04 to 0.36 with arithmetic mean of 0.15. Concerning NP_3, sediment samples provided 0.37 to 0.73 with arithmetic mean of 0.58, while soil samples were found 0.45 to 0.88 with arithmetic mean of 0,58. The contribution from aerosols was ranged from 0.45 to 0.88 with arithmetic mean of 0.67, respectively. These findings suggested that matrices have at least the similar ratio of each isomer to APs which implies that they might have been derived from the similar sources at the same period of input.

Table 5.13. Ratio between NP isomers and total APs in the three differences matrices

(A)	**Aerosols**		
Particle sizes	**NP1/AP**	**NP2/AP**	**NP3/AP**
0.49 - 0.96 µm	0.36	0.36	0.54
0.92 - 1.5 µm	0.1	0.04	0.86
1.5 - 3 µm	0.16	0.07	0.73
3 - 7.2 µm	0.19	0.07	0.73
> 0.72 µm	0.34	0.21	0.45
Average	**0.23**	**0.15**	**0.67**
(B)	**Sediments**		
P1	0.53	0.09	0.37
P4	0.2	0.1	0.69
P5	0.27	0.16	0.57
P12	0.13	0.14	0.73
P10	0.29	0.16	0.55
P11	0.32	0.13	0.54
P7	0.26	0.15	0.6
P8	0.29	0.15	0.56
Average	**0.28**	**0.13**	**0.57**
(C)	**Soils**		
S1	0.1	0.05	0.7
S2	0.07	0.05	0.88
S3	0.14	0.02	0.77
S4	0.12	0.08	0.8
S5	0.1	0.07	0.45
S6	0.16	0.08	0.76
Average	**0.11**	**0.05**	**0.72**

AP = Alkylphenol, NP = Nonylphenol

The presence of APs in sediment was mainly accumulated in the zone where the granular silt concentrated. Whereas, soil samples, particularly within the exposed area of the prevailing wind, the signature of these chemicals were controlled by relief and aerodynamic. The transfer of APs was likely derived from sea surface by the southeast winds toward the surface soils of Creek (Figure 5.12). This is confirmed by aerosol analysis in the zone that showing some differences, a signature of APs consistent and the enrichment in aerosols sizes corresponding to those locally spray.



AP = Alkylphenols, WWTPs = Wastewater treatment plant

Figure 5.12. A model of APs transfer from three different matrices in the vicinity of Cortiou creek stations impacted by emissary point of WWTPs and some local processes.

According to this simple model that we are creating (5.12), it is distinctly described that APs transport, flow out into the oceans, originates from WWTPs discharges. Some proportions of the compounds will slowly drift as the suspended materials and eventually deposited in the sediments. Meanwhile, some will undergo the evaporation due to solar radiation during summer season and float in the air. Since the influence of aerodynamic factors, these particles will be transferred from the air and re-deposited in the land area in accordance with the dominant wind direction blowing during the period. As the earlier explanation that the highest magnitude of APs concentrations are deposited in the area that exposed to the predominantly wind direction. It was previously mentioned that higher APs concentrations bound in soil compared to other matrices such as sediments and aerosols. Similarly to other organics substances like PCBs, are more deposited in soil medium as reported by (Lu et *al* 2016; Cetin *et al* 2017). This is associated with buffering capacity, sorption to hydrophobic organic materials and stability of aggregate which are led to the high capacity of soil particles to bind organic compounds such as APs compared to other compartments (Wershaw 1993). It is important to mention that the three difference compartments, NP_3 were the most abundant isomers found either in sediments, soils or aerosols. The fact that NP_3 observed as the predominantly isomers in this work since the NP_3 isomer consisted of a pair of diastereomers in nearly 1:1 ratio and contained only a trace of the ortho-substituted isomer. In every case, the ortho-substituted isomers are well separated from the major para-NP isomers and did not affect any interpretation of mass spectra (Moeder *et al* 2006).

5.5. Environmental Significance

One of the emergent pollutants released into marine environment and penetrate the marine food web are endocrine disrupting compounds (EDCs) namely Alkylphenols (Nonylphenols, 4-tert-Octylphenols and 4-n-Octylphenols). These substances may interfere with the function of hormones in living organisms (USEPA 2010). APs can induce feminisation or hermaphroditism in animals, whereas cancer in reproductive organs such as the testicles, prostate and mammary glands can be occurred in humans (Markey *et al* 2001; Kang *et al* 2006; Staniszewska *et al* 2016).

These substances can be transferred to the lowest trophic levels, a dynamic which occurs to be important for the locomotion of hydrophobic pollutants up to a higher trophic level particularly in marine ecosystem. Several works reported their accumulation or biodegradation by phytoplankton, zooplankton or bacteria and other benthic organisms (Cailleaud *et al* 2007; Magnusson and Tiselius 2010; Staniszewska *et al* 2016).

To diagnose the environmental significance of APs, we compared our data with consensus based sediments and soil guide lines (PNEC, Predicted Non-Effect Concentration) (European Council 2002; INERIS 2014), these values have been used by Dong *et al* (2014). PNEC for sediments is 39 µg.kg^{-1} dw and soils is 300 µg.kg^{-1} dw, respectively. Our work shows the distribution of APs concentrations within both sediments and soils samples are described in Figure 5.13 and Figure 5.14. Since the concentrations of these compounds at the stations beyond emissary point were discrete we did not include them in this diagnosis. Additionally, 4-tert-OP and 4-n-OP were found in very low concentration thus they were not analysed for PNEC, neither. The concentrations of the three NPs isomers in sediments ranged between 11 to 216.5 µg.kg^{-1} dw with the predominance isomer was NP$_3$ at the stations P5 and P7 which were at the centre of the plume and at the offshore one. Concerning ecological risk, the results suggested a potential adverse effect on marine biota (>39 µg.kg^{-1} dw) due to the majority of the sediments samples (62.92%) exceeded the PNEC value. Regarding soil samples, the concentrations of APs ranged between 3.13 to 396.8 µg.kg^{-1} dw with the maximum concentrations found at the stations S1, S2 and S3 which were situated at the corridor exposed to the predominantly wind direction. A 16% of NPs isomers of soil samples in this coastal zone exceeded PNEC (300 µg.kg^{-1} dw). These findings indicated that there is an adverse effect to organisms in the vicinity of Cortiou Creek. According to this work, in the sediments and soils of Cortiou Creek, it can be speculated that the study area carries an ecological risk. Nonetheless, Roberts *et al* 2006 discovered that these ranges could not pose any negative risks to the plants and organisms in this area unless the magnitudes of these chemicals over 10000 mg.kg^{-1} dw. The concentrations at which NPs can be transported from the soil to the surrounding animals and plants. It is suggested that the uptake of NP by plants is very low. Additionally, when NPs are sorbet to the solid phase, they could easily be leached from soil. Taking all of our results together, we conclude that the spreading of NP in the soil samples probably do not pose any environmental risk to the terrestrial ecosystems and human health.

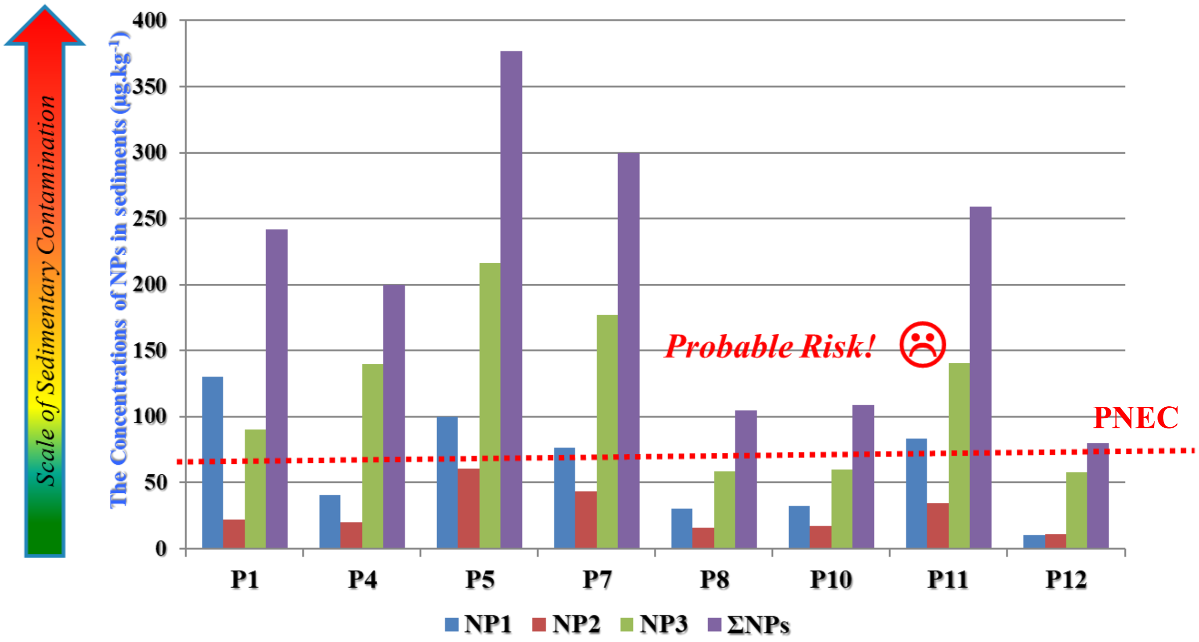


Figure 5.13. Predicted No – Effect Concentration (PNEC) of Nonylphenols in surface sediments from Cortiou Creek, Marseilles.

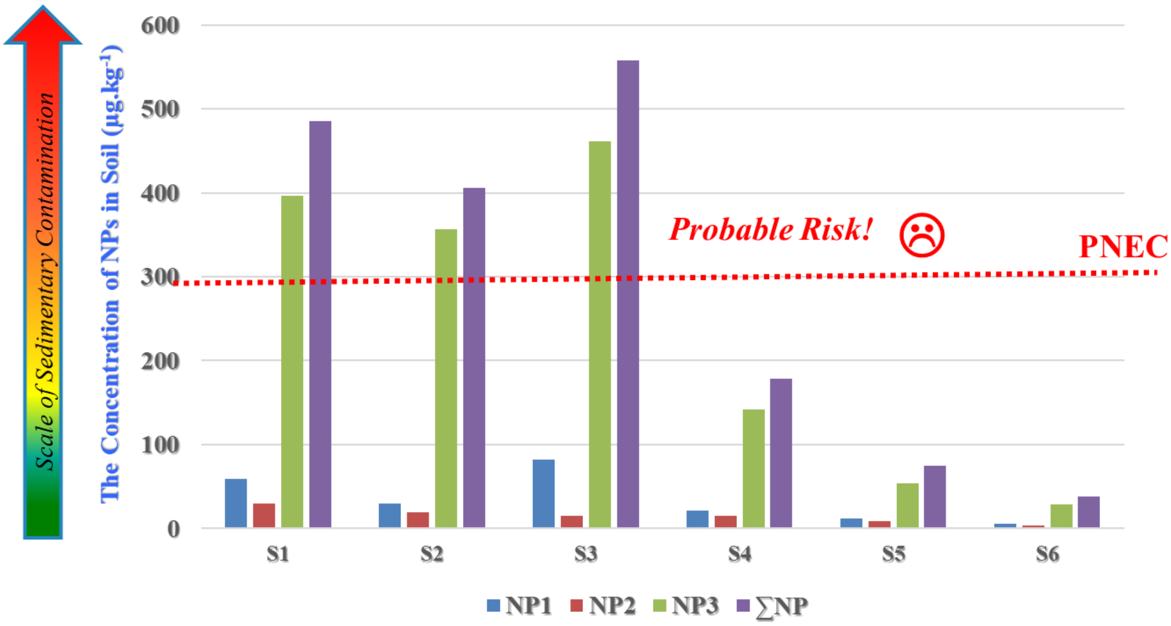


Figure 5.14. Predicted No – Effect Concentration (PNEC) of Nonylphenols in surface soils from Cortiou Creek, Marseilles.

5.6. Conclusion

The three commercial Alkylphenols (NPs, 4-tert-OP, and 4-n-OP) were determined in the three difference compartments in the vicinity of Cortiou Creek, Marseilles Bay. The three isomers of NPs (NP_1, NP_2 and NP_3) were detected within the three difference matrices (sediments, soil and aerosol). Whereas, 4-tert-OP and 4-n-OP were measurable in very low concentrations. Even, the two last commercial of APs were undetectable in several stations. NP_1 and NP_3 were the predominantly NPs which were found in sediments, soil and aerosols with higher concentrations compared to NP_2.

These APs were likely derived from the same sources either directly from emissary point of WWTPs or direct input from other activities such as shipping traffic and domestic discharge.

The coefficient correlation between APs and TOC, particle sizes and Al, Li, Pb shows insignificance relation which suggested that there were other factors supported the settling and distribution of these substances in Cortiou Creek, the Bay of Marseilles.

The highest magnitudes of APs were concentrated at the southeast of the plum due to the prevailing wind induced the deviation of the plum that transported these pollutants to this side.

Based on the Predicted No-Effect Concentrations (PNEC), these concentrations in the sediments exceeded the PNEC value which means they probably pose an adverse effect to the benthic organisms in marine area. On the other hand, in soil, these APs concentrations do not have any impacts to the plants and human health in the vicinity of Cortiou.

Eventually, this research indicated that the most deposited APs was in soil which attributed that the final stored of these substances is presumably in the soils after having had any physical and chemical processes in the other mediums such as water, sediments and air.

Even though the new WWTPs-cleansing unit (Geolide) has been implemented with the last generation process of biological treatment, this work suggested that adverse effects linked to NPs abundance probably happened in sediments and potentially in soils. However, considering first that the surficial sediments integrate a large time span, and second the technical difficulty to obtain sediment cores in this area, it is too early to see the positive effects of the WWTP biological process and it is difficult to predict when this improvement can be highlighted. Hence, in the future, it is necessary to regularly monitor the contamination of soils and sediments in the vicinity of the WWTP.

CHAPTER VI

GENERAL CONCLUSION AND PERSPECTIVE

6.1. Conclusions

The Mediterranean Sea is a semi-closed maritime area which represents only 1% of the surface of the world ocean but hosts nearly 30% of the world's maritime traffic which occupied by 22 countries. Thus, this sea presents a very high population density in terms of littoral population which consists of 450 to 500 million permanent inhabitants and 523 million are predicted in the future (2025).

In addition, the Mediterranean area is visited by around 350 to 400 million tourists each year, bringing the total population to approximately one billion. Therefore, this area is also called the extreme anthropogenic pressure region.

According to this work, it is important to mention that Cortiou Creek with its complex ecosystem is truly fascinating thanks to its biodiversity hot spot. Nevertheless, this area also can be categorized as a hot spot of organic micro-pollutant contamination which is so called the paradoxal site. Therefore, 140 endemic terrestrial and marine species of which 40 being protected are in danger due to the very strong anthropic pressure issued from urban, industrial and tourist activities.

It is believed that Cortiou Creek area is highly contaminated, particularly by hydrocarbon pollution originating from mixed sources (biomass and oil combustion).

Similarly, PCBs, OCPs, and APs which are derived from urban, industrial, domestic and WWTPs activities probably induce toxicity risks for benthic organisms.

Moreover, the littoral soils are also impacted by APs which were probably emitted by WWTPs or directly from domestic and industrial area in the vicinity of Marseille Coastal area.

Concerning APs as emerging pollutants, NP_3 appears to be an effective tracer/indicator of pressure and impact of WWTPs since they were found abundantly in sediments, aerosols and soils.

The tendency of organic micro-pollutant concentrations deposited on the east side of the plume is likely induced by the wind and hydrodynamic processes such as turbulence, upwelling and bathymetry conditions.

The coefficient correlation between APs and TOC, particle sizes and Al, Li, Pb shows insignificance relation which suggested that there were other factors supported the settling and distribution of these substances in Cortiou Creek in the Bay of Marseilles.

Even though the new WWTPs-treatment unit (Geolide) has been implemented with the latest generation process of biological treatment in 2008, this work suggested that there are adverse effects linked to NPs abundance probably happened in sediments and potentially in soils. At the same time, I/E ratio of LABs sedimentary showed that the biodegradation process was largely incomplete. Nevertheles, considering that the surficial sediments cover a large time span, and because there is a technical difficulty to obtain sediment cores in this area, it is therefore too early to reveal the positive impact of the WWTP biological process after 7 years of the geolide functioning.

The high contaminant levels followed by a cumulative concentration of several toxic compounds may increase overall sediment toxicity. Aditionnally, it should be taken into accounts that the ecotoxicity of sediments is most likely understated because each family of contaminants has been assessed individually. Nevertheless, the negative effect of mixtures is now demonstrated. Thus, these findings highlight the necessity to continue environmental monitoring to assess sewage pollution release in coastal areas and determine the level of improvement of one of the ‘‘biggest’’ WWTPs in the world (Géolide). It is necessary to avoid future contaminant discharge into the National Park to ensure a better marine environment.

6.2. Perspectives

It is essential to carry out a monitoring to validate the restoration of the medium following the installation og Géolide.

It is necessary to evaluate the impacts of the aerosols on other contaminants and extend the study geographically.

This study could be enriched by a mathematical model in which the supplementary data such as water, biota and oceanography data are needed to be collected.

It would be a sophisticate information, if the future work was accompanied with other emerging compounds such as pharmaceutical substances and bisphenol A with another analytical devices such as LC/MS/MS.

References

Abdel-Shafy H. I., Mansoer M. S. M. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation.. Egyptian Journal of Petroleum Egyptian Journal of Petroleum. 25, 107–123.

Aboucaya A., Verlaque R., Guyot I. (2001). La conservation des plantes rares et menacées en France. In Gomez-Campo C (ed) Conservation de especies vegetales amenazadas en la region mediterrànean occidental. R Areces Edit 199–227.

Abdur Rehman M.Y., Kamal A., Taqi M.M., Malik R.N. (2017) Tracing biomarker of PAH-exposure and susceptibility factor (GSTM-polymorphism) among cancer patients in Pakistan. Chemosphere 178, 384-390.

Abraham J., Silambarasan S., Logeswari P. (2014). Simultaneous degradation of organophosphorus and organochlorine pesticides by bacterial consortium. J. Taiwan Inst.Chem. Engin. Vol. 45. 2590-2596.

Acquavita A., Falomo J., Predonzani S., Tamberlich F., Bettoso N., Mattassi G. (2014) The PAH level, distribution and composition in surface sediments from a Mediterranean Lagoon: the Marano and Grado Lagoon (Northern Adriatic Sea, Italy). Marine pollution bulletin 81(1), 234-241.

Ademollo N., Patrolecco L., Matozzo V., Marin M.G., Polesello S. (2017). Clam bioaccumulation of Alkylphenols and Polyciclic aromatic hydrocarbons in the Venice lagoon under different pressures. Mar. Pollut. Bullet.Vol.124. 121-129.

Adams B., Gavin C. L., McGowen M. M., Waddell W. J., Smith R. L. (2011). The FEMA GRAS assessment of aliphatic and aromatic terpene hydrocarbons used as flavor ingredients. Food Chem.l Toxicol, Vol. 49. 2471-2494.

Ahmed M. M., Doumenq P., OAwaleh M., Syakti A. D., Chiron S. (2017). Levels and sources of heavy metals and PAHs in sediment of Djibouti-city (Republic of Djibouti). Mar. Pollut. Bullet. Vol. 120. 340-346.

Ahel M., Giger W. (1993) Partitioning of alkylphenols and polyethoxylates between water and organic solvents. Chemosphere 26: 1471-1478.

Ahel M., Scully F. E., Hoigne J., W Giger. (1994). Photochemical degradation of nonylphenol and nonylphenol polyethoxylates in natural waters. Chemosphere 28: 1361-1368.

Aitken C., Head M. I. M., Jones D. M., Rowland S. J. (2018). Comprehensive two-dimensional gas chromatography-mass spectrometry of complex mixtures of anaerobic bacterial metabolites of petroleum hydrocarbons. J. Chrom. Vol. 1536. 96-109.

Akinlua A., Olise F. S., Akomolafe A.O., McCrindle R. I. (2016). Rare earth element geochemistry of petroleum source rocks from northwestern Niger Delta. Marine and Petroleum Geology 77, 409-417.

Akyüz M., Cabuk H. (2010). Gas-particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. Sci Total Environ. 2010 408 (22). 550 - 8.

Akhbarizadeh R., Moore F., Keshavarzi B., Moeinpour A. (2016). Aliphatic and polycyclic aromatic hydrocarbons risk assessment in coastal water and sediments of Khark Island, SW Iran. Mar. Pollut. Bullet. Vol.108. 33-45.

Alonso-Hernández C. M., Tolosa I., Mesa-Albernas M., Díaz-Asencio M., Sánchez-Cabeza J. A. (2015). Historical trends of organochlorine pesticides in a sediment core from the Gulf of Batabanó, Cuba. Chem. Vol.137. 95-100.

Al-Areeq N.M., Al-Badani M.A., Salman A.H., Albaroot M.A. (2018) Petroleum source rocks characterization and hydrocarbon generation of the Upper Jurassic succession in Jabal Ayban field, Sabatayn Basin, Yemen. Egyptian Journal of Petroleum.

Al-Saad H.T. (1987) Distribution of polycyclic aromatic hydrocarbons (PAH) in surficial sediments from Shatt Al-Arab River and the north-west region of the Arabian Gulf. Marine pollution bulletin 18(5), 248-251.

Alegria H., Martinez-Colon M., Birgul A., Brooks G., Kurt-Karakus P. (2016). Historical sediment record and levels of PCBs in sediments and mangroves of Jobos Bay, Puerto Rico. Sci.Tot. Environ. Vol. 573. 1003-1009.

Alkhadher S. A. A., Zakaria M. P., Yusoff F. M., Kannan N., Suratman S., Keshavarzifard M., Magam S. M., Masood N., Vaezzadeh V., Sani M. S. A. (2015). Baseline distribution and sources of linear alkyl benzenes (LABs) in surface sediments from Brunei Bay, Brunei. Mar. Poll. Bull.101. 397 – 403.

Ali N., Ismail I M I., Khoder M., Shamy M., Costa M. (2017). Polycyclic aromatic hydrocarbons (PAHs) in the settled dust of automobile workshops, health and carcinogenic risk evaluation. Sci.Tot. Environ.Vol. 601–602. 478-484.

Amodio-Cocchieri R., Cirillo T. (2003). Aliphatic hydrocarbons in biota from the Gulf of Naples (Italy). Mar. Pollut. Bullet. Vol. 374-377.

Annamalai J., Namasivayam V. (2015). Endocrine disrupting chemicals in the atmosphere: Their effects on humans and wildlife. Environ. Inter. Vol.76.78-97.

Andreu V., Ferrer E., Rubio J. L., Font G., Picó Y. (2007). Quantitative determination of octylphenol, nonylphenol, alkylphenol ethoxylates and alcohol ethoxylates by pressurized liquid extraction and liquid chromatography–mass spectrometry in soils treated with sewage sludges. Sci. Tot. Environ. Vol. 378. 124-129.

Arditsoglou A., Voutsa D. (2008) Determination of phenolic and steroid endocrine disrupting compounds in environmental matrices. Environ Sci Pollut Res 15: 228-236

Assunção M. A., Frena M., Santos A. P. S., Madureira L. A. S. (2017). Aliphatic and polycyclic aromatic hydrocarbons in surface sediments collected from mangroves with different levels of urbanization in southern Brazil. Mar. Pollut. Bullet. Vol. 119. 439-445.

Ashraf A., Saion E., Gharibshahi E., Yap C. K., Rahman S. A. (2018). Distribution of Heavy Metals in Core Marine Sediments of Coastal East Malaysia by Instrumental Neutron Activation Analysis and Inductively Coupled Plasma Spectroscopy. Appli. Rad. Isotop. Vol.132. 222-231.

Asia L., Mazouz S., Guiliano M., Doumenq P., Mille G. (2009) Occurrence and distribution of hydrocarbons in surface sediments from Marseille Bay (France). Mar Pollut Bull 58:424–455.

Asia L. (2012). Analyse des hydrocarbures dans des sédiments superficiels de zones côtières Méditerranéennes (Golfe de Fos, Rade de Marseille et Massif des Calanques). Thèse Doctorate Science de l'Environnement. Aix-Marseille Université. Non-publiée.

Attaullah M., Yousuf M. J., Shaukat S., Anjum S. I., Khan S. U. (2017). Serum organochlorine pesticides residues and risk of cancer: A case-control study. Saudi J. Biolog. Sci. In press, corrected proof, Available online 17 October 2017.

Azzouz A., Rascón A. J., Ballesteros E. (2016). Simultaneous determination of parabens, alkylphenols, phenylphenols, bisphenol A and triclosan in human urine, blood and breast milk by continuous solid-phase extraction and gas chromatography–mass spectrometry. J. Pharma. Biomed. Anal. Vol.119.16-26.

Baumard P., Budzinski H., Michon Q., Garrigues P., Burgeot T., Bellocq J. (1998) Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. Estuarine, Coastal and Shelf Science 47(1), 77-90.

Bapayeva G., Issayeva R., Zhumadilova A., Nurkasimova R., Tleuzhan R. (2016). Organochlorine pesticides and female puberty in South Kazakhstan. Repro. Toxicol. Vol. 65. 67-75.

Banjoo D. R., Nelson P. K. (2005). Improved ultrasonic extraction procedure for the determination of polycyclic aromatic hydrocarbons in sediments. J. Chromato. Vol. 1066. 9-18.

Bai N., Abuduaini R., Wang S., Zhang M., Zhao Y. (2017). Nonylphenol biodegradation characterizations and bacterial composition analysis of an effective consortium NP-M2. Environ. Poll. Vol.220, 95-104.

Balaguer P., Bourguet W. (2018). Toxicant Actions: Mode of Action of Endocrine Disruptors. Ref. Mod.Biomed. Sci.

Barakat A. O., Khairy M., Aukaily I. (2013). Persistent organochlorine pesticide and PCB residues in surface sediments of Lake Qarun, a protected area of Egypt. Chem. Vol. 90. 2467-2476.

Barakat A., Mostafat A., Wade T.L., Sweet S.T., El Sayed N.B., (2011). Distribution and characteristics of PAHs in sediment from the Mediterranean coastal environment of Egypt. Mar. Pollut. Bull., 62, 1969-1978.

Beyer J., Myhre L P., Sundt R. C., Meier S., Sanni S. (2012). Environmental risk assessment of alkylphenols from offshore produced water on fish reproduction. Mar. Environ. Res. Vol. 75. 2-9.

Berkner S., Streck G., Herrmann R. (2004). Development and validation of a method for determination of trace levels of alkylphenols and bisphenol A in atmospheric samples. Chem. Vol. 54. 4. 575-584.

Bennie D., Sullivan T., Lee C. A., Peart H B., Maguire T. (1997). Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the LaurentianGreat Lakes basin and the upper St. Lawrence River. Sci. Tot. Environ.193, 263–275.

Besis A., Tsolakidou A., Balla D., Samara C., Lialiaris T S. (2017). Toxic organic substances and marker compounds in size-segregated urban particulate matter Implications for involvement in the in vitro bioactivity of the extractable organic matter. Environ. Poll.Vol.230. 758-774.

Beyer J., Trannum H C., Bakke T., Hodson P V., Collier T K. (2016). Environmental effects of the Deepwater Horizon oil spill: A review. Mar. Poll. Bull. Vol. 110. 28-51.

Bezza F. A., Chirwa E. M. N. (2016). Biosurfactant-enhanced bioremediation of aged polycyclic aromatic hydrocarbons (PAHs) in creosote contaminated soil. Chem. Vol.144. 635-644.

Bettinetti R., Quadroni S., Boggio E., Galassi S. (2016). Recent DDT and PCB contamination in the sediment and biota of the Como Bay (Lake Como, Italy). Sci. of The Tot. Environ. Vol. 542. 404-410.

Berk I., Ediger V Ş. (2018). A historical assessment of Turkey’s natural gas import vulnerability Energy, Vol. 145. 540-547.

Benson N. U., Fred-Ahmadu O. H., Olugbuyiro J. A. O., Anake W. U., Olajire A. A. (2018). Concentrations, sources and risk characterisation of polycyclic aromatic hydrocarbons (PAHs) in green, herbal and black tea products in Nigeria. J. Food Comp. Anal. Vol. 66. 13-22.

Beriro D. J., Cave M. R., Wragg J., Thomas R., Evans F. (2016). A review of the current state of the art of physiologically-based tests for measuring human dermal in vitro bioavailability of polycyclic aromatic hydrocarbons (PAH) in soil. J. Hazard. Mat. Vol. 305. 240-259.

Bejarano A. C., Michel J. (2016). Oil spills and their impacts on sand beach invertebrate communities: A literature review. Environ. Pollut.Vol. 218. 709-722.

Berna J. L. (1994). Growth and development in LAB technology, 3rd World Detergent Conference, Montreux (CH), Ed. A Cahn, NY 1994, AOCS Press.

Berninger J. P., Brooks B. W. (2010). Leveraging mammalian pharmaceutical toxicology and pharmacology data to predict chronic fish responses to pharmaceuticals. Toxicol. Lett. 193. 69 – 78.

Bertrand J.C., Mille G. (1989). Devenir de la matière organique exogène. Un modèle : les hydrocarbures. In : micro-organismes dans les écosystèmes marins. Bianchi M. Marty, D., Bertrand, J.C., Caumette, P., Gautier, M. . (éd. Masson) Paris, p. 343-373.

Bertrand J.C., Doumenq P., Guyoneaud R., Marrot B., Martin-Laurent F., Matheron R., Moulin P., Soulas G., (2012). Écologie microbienne appliquée et dépollution - les micro-organismes acteurs majeurs de l’élimination des pollutions. Chap. 16 ,705-790. Presses Universitaires de Pau et des pays de l’Adour qui affectent l’environnement en écologie microbienne ; Microbiologie des milieux naturels anthropisés. Ed. Bertrand Jean Claude.

Bhattacharyya A., Sengupta S., Kumar S. (2015). Hydrophobic hydration from solubilities of aliphatic hydrocarbons in water. J. Molecul. Liq.Vol. 204. 176-183.

Bihari N., Fafand M., Hamer B., Kralj-Bilen B. (2006) PAH content, toxicity and genotoxicity of coastal marine sediments from the Rovinj area, Northern Adriatic, Croatia. Science of The Total Environment 366(2-3), 602-611.

Bjoerseth A., Dekker M. (1983). Handbook of polycyclic aromatic hydrocarbons, Emission Sources and Recent Progress in Analytical Chemistry. New York and Basel Vol.1 727 p.

Bjorkland K., Cousins A P., Strmvall A., Malmqvist P. (2009). Phthalates and nonylphenols in urban runoff: Occurrence, distribution and area emission factors. Sci. Tot. Env. 407. 4665 – 4672.

Birch H., Rikke H., Mike C., Philipp M. (2017). Biodegradation of hydrocarbon mixtures in surface waters at environmentally relevant levels – Effect of inoculum origin on kinetics and sequence of degradation. Chem, Vol 184, 400-407.

Bina B., Mohammadi F., Amin M M., Pourzamani H. R., Yavari Z. (2018). Determination of 4-nonylphenol and 4-tert-octylphenol compounds in various types of wastewater and their removal rates in different treatment processes in nine wastewater treatment plants of Iran. Chinese J. Chem. Engin. Vol. 26. 183-190.

Bizarro C., Ros O., Vallejo A., Prieto A., Ortiz-Zarragoitia M. (2014). Intersex condition and molecular markers of endocrine disruption in relation with burdens of emerging pollutants in thicklip grey mullets (Chelon labrosus) from Basque estuaries (South-East Bay of Biscay). Mar. Environ. Res. Vol. 96.19-28.

Blumer M. (1957) Removal of Elemental Sulfur from Hydrocarbon Fractions. Analytical Chemistry 29(7), 1039-1041.

Bleeker E.A.J, Verbruggen E.M.J. (2009). Bioaccumulation of polycyclic aromatic hydrocarbons in aquatic organisms. RIVM report 601779002/2009

Bolden A. L., Rochester J. R., Schultz K., Kwiatkowski C. F. (2017). Polycyclic aromatic hydrocarbons and female reproductive health: A scoping review. Repro. Toxicol. Vol. 73. 61-74.

Boehler S., Lörracher A., Schubert J., Braunbeck T. (2018). Comparative live-imaging of in vivo EROD (ethoxyresorufin-O-deethylase) induction in zebrafish (Danio rerio) and fathead minnow (Pimephales promelas) embryos after exposure to PAHs and river sediment extracts. Sci.Tot. Environ.Vol. 621. 827-838.

Boitsov S., Jensen H.K.B., Klungsøyr J. (2009) Natural background and anthropogenic inputs of polycyclic aromatic hydrocarbons (PAH) in sediments of South-Western Barents Sea. Marine environmental research 68(5), 236-245.

Bojokowska I., Krasuskal J., Retka J., Wilkomirski B. (2013). Lead concentration and the content of selected macroelements in lake sediments in Poland. J. Elem. s. 627–636.

Boonyatumanond R., Wattayakorn G., Togo A., Takada H. (2006) Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. Marine pollution bulletin 52(8), 942-956.

Brulle F., Morgan A. J., Cocquerelle C., Vandenbulcke F. (2010). Transcriptomic underpinning of toxicant-mediated physiological function alterations in three terrestrial invertebrate taxa: A review. Environ. Vol.158. 2793-2808.

Brown D. R., Bailey J.M., Oliveri A.N., Levin E.D., Di Giulio R.T. (2016). Developmental exposure to a complex PAH mixture causes persistent behavioral effects in naive Fundulus heteroclitus (killifish) but not in a population of PAH-adapted killifish. Neurotoxicol. Teratolog. Vol 53. 55-63.

Braga O., Smythe G. A., Schafer A. I., Feitz A. J. (2005). Steroid estrogens in ocean sediments. Chemosphere, 61(6): 827–833.

Bruce G.M., Pleus R.C., Snyder S.A. (2010). Toxicological relevance of pharmaceuticals in drinkingwater. Environ. Sci. Technol. 44 : 5619 – 26.

Brown K. E., King C. K., Kotzakoulakis K,. George S. C., Harrison P. L. (2016). Assessing fuel spill risks in polar waters: Temporal dynamics and behaviour of hydrocarbons from Antarctic diesel, marine gas oil and residual fuel oil. Mar. Poll. Bullet. Vol. 110. 343-353.

Buah-Kwofie A., Humphries M S. (2017). The distribution of organochlorine pesticides in sediments from iSimangaliso Wetland Park: Ecological risks and implications for conservation in a biodiversity hotspot. Environ. Poll.Vol. 229. 715-723.

Buurman P., de Boer K., Pape T. (1997) Laser diffraction grain-size characteristics of Andisols in perhumid Costa Rica: the aggregate size of allophane. Geoderma 78(1), 71-91.

Cachot J., Geffard O., Augagneur S., Lacroix S., Le Menach K., Peluhet L., Couteau J., Denier X., Devier M., Pottier D. (2006) Evidence of genotoxicity related to high PAH content of sediments in the upper part of the Seine estuary (Normandy, France). Aquatic toxicology 79(3), 257-267.

Cachada A., Pato P., Rocha-Santos T., Ferreira da Silva E., Duarte A. C. (2012). Levels, sources and potential human health risks of organic pollutants in urban soils. Science of The Total Environment, Volume 430, 15 July 2012, Pages 184-192

Canada (2002). Environment Canada. Canadian Environmental Quality Guidelines for Nonylphenol and its Ethoxylates (Water, Sediment, and Soil) Scientific Supporting Document. Ecosystem Health: Science-based Solutions Report No. 1-3. National Guidelines and Standards Office, Environmental Quality Branch, Environment Canada.

Cancer I.A.R.C (2010) Alcohol consumption and ethyl carbamate, IARC Press, International Agency for Research on Cancer.

Chiu T.R., Nanyan N.F.M., Ali M.M. (2015) Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Sediments of Kapas Island, Terengganu, Malaysia. Procedia Environmental Sciences 30, 162-167.

Chung S.H., Ding W.H. (2018) Isotope-dilution gas chromatography-mass spectrometry coupled with injection-port butylation for the determination of 4-t-octylphenol, 4-nonylphenols and bisphenol A in human urine. Journal of pharmaceutical and biomedical analysis 149, 572-576.

Culotta L., De Stefano C., Gianguzza A., Mannino M.R., Orecchio S. (2006) The PAH composition of surface sediments from Stagnone coastal lagoon, Marsala (Italy). Marine Chemistry 99(1-4), 117-127.

Cavalli L., Clerici P., Radici L., Valtorta (1999b). Update on LAB/LAS, Tenside Surf. Det.36: 254-258

Chakraborty P., Zhang G., Li J., Sivakumar A., Jones K. C. (2015). Occurrence and sources of selected organochlorine pesticides in the soil of seven major Indian cities: Assessment of air–soil exchange. Environ. Poll. Vol. 204. 74-80.

Cardellicchio N., Buccolieri A., Giandomenico S., Lopez L., Pizzulli F., Spada L. (2007) Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian sea, Southerne Italy). Mar. Pollu. Bull. 55: 451-458.

Cowie A. M., Sarty K. I., Mercer A., Koh J., Martyniuk Ch. J. (2017). Molecular networks related to the immune system and mitochondria are targets for the pesticide dieldrin in the zebrafish (Danio rerio) central nervous system. Journ. of Proteo. Vol. 157. 71-82.

Combarnous Y. (2017). Endocrine Disruptor Compounds (EDCs) and agriculture: The case of pesticides. Comptes Rendus Biologies, Vol. 340. 406-409.

Cao M., Tu S., Xiong S., Zhou H., Lu X. (2018). EDDS enhanced PCB degradation and heavy metals stabilization in co-contaminated soils by ZVI under aerobic condition. J. Hazard. Mat. Vol. 358. 265-272.

Chen H. J., Tseng D. H., Huang S. L. (2005). Biodegradation of octylphenol polyethoxylate surfactant Triton X-100 by selected microorganisms. Biores. Tech. 96.1483-91.

Chen B., Mai B., Duan J., Luo X., Fu J. (2005). Concentrations of alkylphenols in sediments from the Pearl River estuary and South China Sea, South China. Mar. Pollut. Bullet. Vol. 50. 993-997.

Couderc M., Poirier L., Zalouk-Vergnoux A., Kamari A., Le Bizec B. (2015). Occurrence of POPs and other persistent organic contaminants in the European eel (Anguilla anguilla) from the Loire estuary, France. Sci. Tot. Environ. Vol. 505.199-215.

Cailleaud K., Forget-Leray J., Souissi S., Hilde D., Budzinski H. (2007). Seasonal variations of hydrophobic organic contaminant concentrations in the water-column of the Seine Estuary and their transfer to a planktonic species Eurytemora affinis (Calanoïda, copepoda). Part 1: PCBs and PAHs. Chem. Vol. 70. 270-280.

Chevreuil M. (2009). Agence de leau Seine-Normandie, Programme Interdisciplinaire De Recherche Sur L'environnement De La Seine, La micropollution organique dans le bassin de la Seine: maîtriser l' impact des molécules créées pa l'homme, Agence de l'eau Seine-Normandie.

Chalaux N., Bayona J.M., Vankatesan M.I., Albaigues J., (1992). Distribution of surfactant markers in sediments from Santa Monica basin, Southern California. Mar. Pollut. Bull., 24 (8), 403-407.

Clarke A. D., Owens S R., Zhou J. (2005). An ultrafine sea-salt flux from breaking waves: Implications for cloud condensation nuclei in the remote marine atmosphere. J Geophys. Res. Vol 111.

Cachada A., Pato P., Rocha-Santos T., Ferreira da Silva E., Duarte A. C. (2012). Levels, sources and potential human health risks of organic pollutants in urban soils. Sci. Total Environ. Vol. 430. 184-192.

Cacciatore F., Bernarello V., Brusà R. B, Sesta G., Lamberti C. V. (2018). PAH (Polycyclic Aromatic Hydrocarbon) bioaccumulation and PAHs/shell weight index in Ruditapes philippinarum (Adams & Reeve, 1850) from the Vallona lagoon (northern Adriatic Sea, NE Italy). Ecotoxicol. Environ. Safe.Vol.148.787-798.

Cocci P., Mosconi G., Bracchetti L., Nalocca J. M., Palermo F. A. (2018). Investigating the potential impact of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) on gene biomarker expression and global DNA methylation in loggerhead sea turtles (Caretta caretta) from the Adriatic Sea. Sci. Tot. Environ.Vol. 619–620. 49-57.

Cetin B., Yurdakul S., Gungormus E., Ozturk F., Sofuoglu S. C. (2018). Source apportionment and carcinogenic risk assessment of passive air sampler-derived PAHs and PCBs in a heavily industrialized region. Sci.Tot. Environ. Vol. 633. 30-41.

Çok I., Mazmanci B., Mazmanci M. A., Turgut C., Schramm K. (2012). Analysis of human milk to assess exposure to PAHs, PCBs and organochlorine pesticides in the vicinity Mediterranean city Mersin, Turkey. Environ. Inter. Vol. 40. 63-69.

Chávez-Rodríguez M. F., Garaffa R., Andrade G., Cárdenas G., Lucena A. F. P . (2016). Can Bolivia keep its role as a major natural gas exporter in South America? J. Nat. Gas Sci. Engin. Vol. 33, 717-730.

Crespo M. O. P., Yusty M. A. L. (2004). Determination of aliphatic hydrocarbons in the alga Himanthalia elongate. Ecotoxicol. Environ. Safe. Vol. 57. 226-230.

Ciofi L., Ancillotti V., Chiuminatto U., Fibbi D., Checchini L., Orlandini S., Del Bubba M. (2014). Liquid chromatographic-tandem mass spectrometric method for the simultaneous determination of alkylphenols polyethoxylates, alkylphenoxy carboxylates and alkylphenols in wastewater and surface-water. J Chromatogr A. 1362.75-88.

Céspedes R., Lacorte S., Ginebreda A., Barcelo D. (2007). Occurrence and Fate of Alkylphenols and Alkylphenol Ethoxylates in Sewage Treatment Plants and Impact on Receiving Waters along the Ter River (Catalonia, NE Spain). Environ. Poll. 153. 384-92.

Chen J., Zhang W., Li S., Zhang F., Huang X. (2018). Identifying critical factors of oil spill in the tanker shipping industry worldwide. J. Clean. Product. Vol. 180. 1-10.

Cecinato A., Guerriero E., Balducci C., Muto V. (2014). Use of the PAH fingerprints for identifying pollution sources. Urb. Climat. Vol. 10. 630-643.

Chávez-Rodríguez M. F., Dias L., Simoes S., Seixas J., Lucena A. F. P. (2017). Modelling the natural gas dynamics in the Southern Cone of Latin America. Appl. Energ. Vol. 201. 219-239

Chung S., DingV. (2018). Isotope-dilution gas chromatography-mass spectrometry coupled with injection-port butylation for the determination of 4-t-octylphenol, 4-nonylphenols and bisphenol A in human urine. J. Pharma. Biomed. Anal. Vol.149. 572-576.

Cheng Z., Dong F., Xu J., Liu X., Zheng Y. (2016). Atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry for simultaneous determination of fifteen organochlorine pesticides in soil and water. Journ. of Chrom. Vol. 1435. 115-124.

Chen L., Feng Q., He Q., Huang Y., Xu Z. (2017). Sources, atmospheric transport and deposition mechanism of organochlorine pesticides in soils of the Tibetan Plateau. Sci. of The Tot. Environ. Vol. 577. 405-412

COHIBA Guidance Document No. 6, (2011). Measures for emission reduction of nonylphenol (NP) and nonylphenol ethoxylates (NPE) in the Baltic Sea area. COHIBA Proj Consort.

COHIBA Guidance Document No. 7, (2011). COHIBA Guidance Document No.7 for octylphenol (OP) and octylphenol ethoxylates (OPE) in the Baltic Sea area. COHIBA Proj Consort

Dasgupta S., Meisner C., Wheeler D., Xuyen K., Lam N. T. (2007). Intern. Journ of Hygien. and Environ. Health. Vol. 210. 121-132.

Daughton C. G., Ternes T. A. (1999). Pharmaceuticals and personal careproducts in the environment: agents of subtle change? Environ Health Perspect 107 : 907. 37

Dai W., Zhong H., Li L., Cao J., Ho K. F. (2018). Characterization and health risk assessment of airborne pollutants in commercial restaurants in northwestern China: Under a low ventilation condition in wintertime. Sci. Tot. Environ. Vol. 633. 308-316.

Dang V. D., Kroll K. J., Supowit S. D., Halden R. U., Denslow N D. (2018). Activated carbon as a means of limiting bioaccumulation of organochlorine pesticides, triclosan, triclocarban, and fipronil from sediments rich in organic matter. Chem.Vol.197. 627-633.

Dat N., Chang M. B. (2017). Review on characteristics of PAHs in atmosphere, anthropogenic sources and control technologies. Sci. Tot. Environ. Vol. 609. 682-693.

Dachs J., Bayona J. M., Ittekkot V., Albaigés J. (1999). Monsoon-Driven Vertical Fluxes of Organic Pollutants in the Western Arabian Sea. Environ. Sci. Technol., 1999, 33 (22). 3949–3956.

Dachs J., Eisenreich S.J., Baker J.E., Ko F.C., Jeremiason J.D. (1999b). Coupling of phytoplankton uptake and air–water exchange of persistent organic pollutants. Environ. Sci. Technol. 33 (20), 3653–3660.

Dachs J., Lohmann R., Ockenden W.A., Méjanelle L., Eisenreich S.J., Jones K.C., (2002). Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. Environmental Science and Technology 36 (20), 4229–4237.

Dang V.D., Kroll K.J., Supowit S.D., Halden R.U., Denslow N.D. (2018) Activated carbon as a means of limiting bioaccumulation of organochlorine pesticides, triclosan, triclocarban, and fipronil from sediments rich in organic matter. Chemosphere 197, 627-633.

da Silva A.M.F., Pavesi T., Rosa A.C.S., dos Santos T.P., de Medeiros Tabalipa M., Lemes V.R.R., Alves S.R., de Novaes S. P. (2016) Organochlorines and polychlorinated biphenyl environmental pollution in south coast of Rio De Janeiro state. Marine pollution bulletin 108(1-2), 325-331.

Demirtepe H., Kjellerup B., Sowers K. R., Imamoglu I. (2015). Evaluation of PCB dechlorination pathways in anaerobic sediment microcosms using an anaerobic dechlorination model. J. Hazard. Mat. Vol. 296. 120-127.

Dévier M. H., Le Menach K., Viglino L., Di Gioia L., Lachassagne P., Budzinski H. (2013). Ultra-trace analysis of hormones, pharmaceutical substances, alkylphenols and phthalates in two French natural mineral waters. Sci Total Environ. 443. 621-32.

de Mora S., Tolosa I., Fowler S.W., Villeneuve J. P., Cassi R., Cattini C. (2010) Distribution of petroleum hydrocarbons and organochlorinated contaminants in marine biota and coastal sediments from the ROPME Sea Area during 2005. Marine pollution bulletin 60(12), 2323-2349.

de Oliveira Galvão M.F., de Oliveira Alves N., Ferreira P.A., Caumo S., de Castro Vasconcellos P., Artaxo P., de Souza Hacon S., Roubicek D.A., Batistuzzo de Medeiros S.R. (2018) Biomass burning particles in the Brazilian Amazon region: Mutagenic effects of nitro and oxy-PAHs and assessment of health risks. Environmental Pollution 233, 960-970.

Directive (2003)/53/EC Amending for the 26th Time the Council Directive 76/769/EEC Relating to Restrictions on the Marketing and Use of Certain Dangerous Substances and Preparations (Nonylphenol, Nonylphenol Ethoxylates and Cement), European Parliament and the Council of the European Union, Luxembourg, Luxembourg, 2003.

Dong C., Chen C., Chen C. (2015). Seasonal and spatial distribution of 4-nonylphenol and 4-tert-octylphenol in the sediment of Kaohsiung Harbor, Taiwan. Chem. Vol.134. 588-597

Dong C., Chen C., Chen C. (2012). Determination of Polycyclic Aromatic Hydrocarbons in Industrial Harbor Sediments by GC-MS. Int. J. Environ. Res. Public Health 6. 2175-2188.

Doney S. C. (2010). The growing human footprint on coastal and open-ocean biogeochemistry. Science 328.1512 – 6.

Dsikowitzky L., Nordhaus I., Andarwulan N., Irianto H.E., Lioe H.N., Ariyani F., Kleinertz S., Schwarzbauer J. (2016) Accumulation patterns of lipophilic organic contaminants in surface sediments and in economic important mussel and fish species from Jakarta Bay, Indonesia. Marine pollution bulletin 110(2), 767-777.

Duan J., Liu W., Zhao X., Han Y., O'Reilly S., Zhao D. (2018) Study of residual oil in Bay Jimmy sediment 5 years after the Deepwater Horizon oil spill: Persistence of sediment retained oil hydrocarbons and effect of dispersants on desorption. Science of The Total Environment 618, 1244-1253.

Duan X., Li,Y., Li X., Zhang D., Gao Y. (2014) Alkylphenols in surface sediments of the Yellow Sea and East China Sea inner shelf: occurrence, distribution and fate. Chemosphere 107, 265-273.

Dujmov J., Sucevic P. (1990) The Contamination of Dateshell(Lithophaga lithophaga) from the Eastern Coast of the Adriatic Sea by Polycyclic Aromatic Hydrocarbons. Acta Adriatica AADRAY 31(1/2).

Duodu G.O., Goonetilleke A., Ayoko G.A., (2017) Factors influencing organochlorine pesticides distribution in the Brisbane River Estuarine sediment, Australia. Marine pollution bulletin 123(1-2), 349-356.

Dumanoglu Y., Gaga E O., Gungormus E., Sofuoglu S. C., Odabasi M. (2017). Spatial and seasonal variations, sources, air-soil exchange, and carcinogenic risk assessment for PAHs and PCBs in air and soil of Kutahya, Turkey, the province of thermal power plants. Sci. of The Tot. Environ. Vol. 580. 920-935.

Duan X., Wang X., Xie J., Feng L., Zhou Q. (2018). Acidogenic bacteria assisted biodegradation of nonylphenol in waste activated sludge during anaerobic fermentation for short-chain fatty acids production. Biores. Tech.Vol. 268. 692-699.

Dutta S. K., Ghosh S., Eric S.D., Hoffman P. (2008). CYP1A1 and MT1K are congener specific biomarker genes for liver diseases induced by PCBs. Environ. Toxicol. and Pharmacol, Vol. 25. 2. 218-221.

Duan J., Liu W., Zhao X., Han Y., Zhao D. (2018). Study of residual oil in Bay Jimmy sediment 5 years after the Deepwater Horizon oil spill: Persistence of sediment retained oil hydrocarbons and effect of dispersants on desorption. Sci. Tot. Environ. Vol. 618. 1244-1253.

Dwiyitno L., Dsikowitzky I., Nordhaus N., Andarwulan H. E., Irianto H. N., Lioe Ariyani F., Kleinertz S., Schwarzbauer J. (2016). Accumulation patterns of lipophilic organic contaminants in surface sediments and in economic important mussel and fish species from Jakarta Bay, Indonesia Mar. Poll. Bull. 110. 767–777.

Elyasi S. (2016) Petroleum source-rock potential of the Piranj oil field, Zagros basin. Marine and Petroleum Geology 78, 448-454.

El Nemr A.,. El-Sadaawy M. M. (2016). Polychlorinated biphenyl and organochlorine pesticide residues in surface sediments from the Mediterranean Sea (Egypt). Inter. J. Sed. Res. Vol. 31. 44-52.

Eganhouse R. P., Blumfield D. L., Kaplan I. R. (1983). Long-chain alkylbenzenes as moleculartracers of domestic wastes in the marine environment. Environ Sci Tech 1983;17:523–30.

Eganhouse R. P., Sherblom P. M. (2001). Anthropogenic organic contaminants in the effluent of acombined sewer overflow: impact on Boston Harbor. Mar. Environ. Res. 51.51–74.

Eganhouse R. P., Olaguer D. P., Gould B., Phinney C. S. (1988). Use of molecular markers for the detection of municipal sewage sludge at sea. Mar. Environ. Res. 25. 1–22.

Erstfeld K. M., Snow-Ashbrook J. (1999). Effects of chronic low-level PAH contamination on soil invertebrate communities. Chem. Vol. 39. 2117-2139.

Ewence A., Brescia S., Johnson I., Rumsby P. C. (2015). An approach to the identification and regulation of endocrine disrupting pesticides. Food and Chem. Toxicol. Vol. 78. 214-220.

Elbetieha A., Da’as S. I., Khamas W., Darmani H. (2001). Evaluation of the Toxic Potentials of Cypermethrin Pesticide on Some Reproductive and Fertility Parameters in the Male Rats. Arch. Environ. Contam. Toxicol. 41, 522–528.

European Commission, Directive 2004/107/EC of the European Parliament and of the Council of 15 December (2004) relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. J L 023. 0003 – 0016 (26/01/2005).

European Commission (2000) Directive 2000/60/EC of the European Parliament and of the council of 23 October 2000 establishing a Framework for Community action in the field of water policy. Official Journal of the European Communities L327: 1-72.

European Commission (2006) Proposal for a Directive of the European Parliament and of the council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC. Commission of the European Communities, Brusel.

EU (2000): 2000/60/EC of the European Parliament and of the Council establishing a Framework for Community action in the field of water policy. Official Journal of the European Union, Luxembourg.

EU (2001) Decision No. 2455/2001/EC of the European Parliament and of the Council establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC.

EU (2008): Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC.

Erickson L. C., Banerji A., Fritsh T.R., Berna J. L. (1996). New solid-bed alkylation technology for LAB, 4th Cesio World Surfactants CongressV.1, 177, Barcelona, Spain.

Fang H., Dong B., Yan H., Tang F., Yu Y. (2010). Characterization of a bacterial strain capable of degrading DDT congeners and its use in bioremediation of contaminated soil. J. Hazard. Mat.Vol. 184. 281-289.

Fang H., Cai L., Yang Y., Ju F., Zhang T. (2014). Metagenomic analysis reveals potential biodegradation pathways of persistent pesticides in freshwater and marine sediments. Sci. Tot. Environ. Vol. 470–471. 983-992.

Fent K., Weston A. A., Caminada D. (2006). Ecotoxicology of human pharmaceuticals. Aquat. Toxicol. 76:122 - 59.

Ferrara F., Ademollo N., Orrù M A., Silvestroni L., Funari E. (2011). Alkylphenols in adipose tissues of Italian population. Chem.Vol. 82. 1044-1049.

Ferrante M., Zanghì G., Cristaldi A., Copat C., Conti G. O. (2018). PAHs in seafood from the Mediterranean Sea: An exposure risk assessment. Food. Chem. Toxicol. Vol. 115. 385-390.

Fiedler S., Foerster M., Glaser B., Zech W. (2007). Alkylphenols in sediments of the Atlantic Rainforest south-west of São Paulo, Brazil. Chem. Vol. 66. 212-218.

Fritcher D. L., Mazet J. A. K., Ziccardi M. H., Gardner I. A. (2002). Evaluation of two direct immunoassays for rapid detection of petroleum products on marine birds. Mar. Pollut. Bullet. Vol. 44. 388-395.

Fraysse M., Pinazo C., Faure V. M., Fuchs R., Lazzari P., Raimbault P., Pairaud I. (2013). Development of a 3D coupled physical-biogeochemical model for the Marseille coastal area (NW Mediterranean Sea): what complexity is required in the coastal zone? PLoS One. 2013 Dec 4;8(12)

Franco C. F. J., de Resende M. F., de A Furtado L., Brasil T. F., Netto A. D. P. (2017). Polycyclic aromatic hydrocarbons (PAHs) in street dust of Rio de Janeiro and Niterói, Brazil: Particle size distribution, sources and cancer risk assessment. Sci. Tot. Environ. Vol. 599–600. 305-313.

Fu C., Wu S. (2006). Seasonal variation of the distribution of PCB in sediments and biota in a PCB contaminated estuary. Chem. 62: 1786-1794

Fung C. N., Zheng G. J., Connell D. W., Zhang X., Lam P. K. S. (2005). Risks posed by trace organic contaminants in coastal sediments in the Pearl River Delta, China. Mar. Pollut. Bullet. Vol.50. 1036-1049.

Galvão M., de O F., de O Alves N., Ferreira P A., Caumo S., de Medeiros S. R. B. (2018). Biomass burning particles in the Brazilian Amazon region: Mutagenic effects of nitro and oxy-PAHs and assessment of health risks Environmental Pollution, Vol. 233. 960-970.

Gao P., Zhao Y., Ni H. (2018). Incidence of real-world automotive parent and halogenated PAH in urban atmosphere. Environ. Pollut. Vol. 237. 515-522.

Gaines T.B., Linder R.E. (1986). Acute toxicity of pesticides in adult and weanling rats. Fundamen. and Appli. Toxicol. Vol. 7. 299-308.

García-Alvarez N., Martín V., Fernández A., Almunia J., Luzard O. P. (2014). Levels and profiles of POPs (organochlorine pesticides, PCBs, and PAHs) in free-ranging common bottlenose dolphins of the Canary Islands, Spain. Sci. Tot. Environ. Vol. 493. 22-31.

García-Cruz N. U., Sánchez-Avila J. I., Valdés-Lozano D., Gold-Bouchot G., Aguirre-Macedo L. (2018). Biodegradation of hexadecane using sediments from rivers and lagoons of the Southern Gulf of Mexico. Mar. Poll. Bull.Vol.128. 202-207

Gibson R. W., Wang M. J., Padgett E., Beck A. J. (2005). Analysis of 4-nonylphenols, phthalates, and polychlorinated biphenyls in soils and biosolids. Chem. 61.1336 – 1344.

Giuliani S., Piazza R., El Moumni B., Polo F. P., Bellucci L. G. (2015). Recognizing different impacts of human and natural sources on the spatial distribution and temporal trends of PAHs and PCBs (including PCB-11) in sediments of the Nador Lagoon (Morocco). Sci. Tot. Environ. Vol. 526. 346-357.

Golovko O., Kumar V., Fedorova G., Randak T., Grabic R. (2014). Removal and seasonalvariability of selected analgesics/anti-inflammatory,anti-hypertensive/cardiovascular pharmaceuticals and UV filters inwastewater treatment plant, Environ. Sci. Pollut. R. 21 (2014) 7578–7585

Gope M., Masto R. E., George J., Balachandran S. (2018). Exposure and cancer risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the street dust of Asansol city, India. Sustain. Cities Soc. Vol. 38. 616-626.

Goda Y., Kobayashi A., Fujimoto S., Toyoda Y., Miyagawa K., Ike M., Fujita M. (2004). Development of enzyme-linked immunosorbent assay for detection of alkylphenol polyethoxylates and their biodegradation products. Water Res. 38 (20). 4323-30.

Grilo T. F., Cardoso P. G., Pato P., Duarte A. C., Pardal M A. (2014). Uptake and depuration of PCB-153 in edible shrimp Palaemonetes varians and human health risk assessment. Ecotoxicol, Environ. Safe. Vol.101. 97-102.

Grześkowiak T., Czarczyńska-Goślińska B., Zgoła-Grześkowiak A. (2016). Current approaches in sample preparation for trace analysis of selected endocrine-disrupting compounds: Focus on polychlorinated biphenyls, alkylphenols, and parabens. TrAC Trend. Anal. Chem. Vol. 75. 209-226.

Grung M., Petersen K., Fjeld E., Allan I., Ranneklev S. (2016). PAH related effects on fish in sedimentation ponds for road runoff and potential transfer of PAHs from sediment to biota. Sci. Tot. Environ. Vol. 566–567.1309-1317.

Gope M., Masto R. E, George J., Balachandran S. (2018). Exposure and cancer risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the street dust of Asansol city, India. Sustain. Cit. Soc. Vol. 38. 616-626.

Gras J. L., Ayers G. P. (1983). Marine aerosol at southern mid-latitudes Journal of Geophysical Research: Oceans. https://doi.org/10.1029/JC088iC15p10661.

Geever M., Colin D., O'Dowd S. E., Flanagan R., Nilsson E. D., de Leeuw G., Rannik U. (2005). Submicron sea spray fluxes. Geophys. Res. Atmo. Sci. https://doi.org/10.1029/2005GL023081.

Gevao B., Porcelli M., Rajagopalan S., Krishnan D., Zafar J. (2018). Spatial and temporal variations in the atmospheric concentrations of "Stockholm Convention" organochlorine pesticides in Kuwait. Sci. of The Tot. Environ. Vol. 622–623. 1621-1629.

George J, Y Shukla. 2011. Pesticides and cancer: Insights into toxicoproteomic-based findings Journ. of Proteo. Vol. 74. 2713-2722.

Gore A. C., Chappell V.A., Fenton S.E., Flaws J.A., Nadal A.,. Prins G.S., Toppari J., Zoeller R.T. (2015). EDC-2: the endocrine Society's second scientific statement on endocrine-disrupting chemicals Endocr. Rev., 36. E1-E150.

Gong J., Rana Y., Chen D., Yang Y. (2011). Occurrence of endocrine-disrupting chemicals in riverine sediments from the Pearl River Delta, China. Mar. Poll. Bull. Vol. 63. 556-563.

Grandjean P., Landrigan P.J. (2006). Developmental neurotoxicity of industrial chemicals Lancet, 368. 2167-2178.

Green D. L., Stull J. K., Heesen T. C. (1986). Determination chlorinated hydrocarbons in coaslal waters using a moored in situ sampler and transplanted livc mussels. Mar. Poll. Bull. 17, 324-329.

Grimm F. A., Hu D., Kania-Korwel I., Lehmler H.J., Ludewig G., Hornbuckle K.C., Duffel M.W., Bergman A., Robertson L.W. (2015). Metabolism and metabolites of polychlorinated biphenyls Crit. Rev. Toxicol., 45. 245-272.

Grimm N. B., Faeth S. H., Golubiewski N. E., Redman C. L., Wu J. G., Mei B. X. (2008). Global change and the ecology of cities. Sci. 319. 756–760.

Grung M., Petersen K., Fjeld E., Allan I., Ranneklev S. (2016). PAH related effects on fish in sedimentation ponds for road runoff and potential transfer of PAHs from sediment to biota. Sci. Tot. Environ. Vol. 566–567. 1309-1317.

Gupta H. (2018). PAH determination in effluent and sludge samples of paper industry. Environ. Technol. Innov. Vol. 9. 115-121.

Gu Y. G., Li H. B., Lu H. B. (2017) Polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the largest deep plateau lake in China: Occurrence, sources and biological risk. Ecological Engineering 101, 179-184.

Hardell S., Hanna T., Welfinger-Smith G., Burger J., Carpenter D. O. (2010). Levels of Polychlorinated Biphenyls (PCBs) and Three Organochlorine Pesticides in Fish from the Aleutian Islands of Alaska. Vol. 5 Issue 8. e12396.

Harikrishnan N., Ravisankar R., Chandrasekaran A., Gandhi M.S., Kanagasabapathy K., Prasad M., Satapathy K. (2017) Assessment of heavy metal contamination in marine sediments of east coast of tamil nadu affected by different pollution sources. Marine pollution bulletin 121(1-2), 418-424.

Harman C., Thomas K. V., Tollefsen K. E., Meier S., Grung M. (2009). Monitoring the freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAH) and alkylphenols (AP) around a Norwegian oil platform by holistic passive sampling. Mar.Pollut. Bull. Vol.58.1671-1679.

Hartmann P. C., Quinn J., King J. W., Takada H. (2000). Intercalibration of LABs in marine sediment SRM1941 and their application as a molecular marker in Narragansett Bay sediments. Environ. Sci. Tech. 34. 900–6.

Harvey H. R., Taylor K. A., Pie H. V., Mitchelmore C. L. (2014). Polycyclic aromatic and aliphatic hydrocarbons in Chukchi Sea biota and sediments and their toxicological response in the Arctic cod, Boreogadus saida. D. Sea Res. Part II: Topical Studies in Oceanography. Vol. 102 32-55.

Harvey H. R.,. Taylor K. A. (2017). Alkane and polycyclic aromatic hydrocarbons in sediments and benthic invertebrates of the northern Chukchi Sea. Deep Sea Research Part II: Topical Studies in Oceanography. Vol.144. 52-62.

Hamid N., Syed J. H., Junaid M., Mahmood A., Malik R. N. (2018). Elucidating the urban levels, sources and health risks of polycyclic aromatic hydrocarbons (PAHs) in Pakistan: Implications for .changing energy demand. Sci. Tot. Environ. Vol. 619–620.165-175.

Hafeznia H., Pourfayaz F., Maleki A. (2017). An assessment of Iran's natural gas potential for transition toward low-carbon economy. Renew. Sustain. Energ. Reviews, Vol. 79.71-81.

Harikrishnan N., Ravisankar R., Chandrasekaran A., Gandhi M. S., Satapathy K. K. (2017). Assessment of Heavy Metal Contamination in Marine Sediments of East Coast of Tamil Nadu Affected by Different Pollution Sources. Mar. Pollut. Bullet. Vol.121. 418-424.

Han Y., Nambi I. M., Clement T. P. (2018). Environmental impacts of the Chennai oil spill accident – A case study. Sci.Tot. Environ. Vol. 626. 795-806.

Harman C., Thomas K. V., Tollefsen K. E., Meier S., Grung M. (2009). Monitoring the freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAH) and alkylphenols (AP) around a Norwegian oil platform by holistic passive sampling. Mar.Pollut. Bull. Vol.58.1671-1679.

Hardoy J. E., Mitlin D., Satterthwaite D. (2001). Environmental problems in an urbanization world. London : Earthscan.

Hawrelak M., Bennett E., Metcalfe C. (1999). The environmental fate of the primary degradation products of alkylphenol ethoxylate surfactants in recycled paper sludge. Chem. Vol. 39. 745-752

Hamers T., Kamstra J.H, Cenijn P.H., Pěnčíková K., Pálková L., Šimečková P., Vondráček J., Andersson P.L., Stenberg M., Machala M. (2011). In vitro toxicity profiling of ultrapure non-dioxin-like polychlorinated biphenyl congeners and their relative toxic contribution to PCB mixtures in humans. Toxicol. Sci., 121. 88-100.

Hamadache M., Benkortbi O., Hanini S., Amrane A., Moussa Ch.. (2016). A Quantitative Structure Activity Relationship for acute oral toxicity of pesticides on rats: Validation, domain of application and prediction. Journ. of Hazard. Material. Vol. 303. 28-40.

Haneen A., Mohamed G., Abdel-Razek A. S., El Nahas A. F., Mahmoud S. (2017). Assessment of complex water pollution with heavy metals and Pyrethroid pesticides on transcript levels of metallothionein and immune related genes. Fish & Shellfish Immunolog, Vol. 68. 318-326.

He J., Peng T, Yang X., Liu H. (2018). Development of QSAR models for predicting the binding affinity of endocrine disrupting chemicals to eight fish estrogen receptor. Ecotoxicol. Environ. Safe.Vol. 148. 211-219.

Heywood E., Wright J., Wienburg C. L., Black H. I. J., Long S. M., Osborn D. (2006). Factors influencing the national distribution of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in British soils. Environ. Sci. Tech. 40.7629 – 35.

Heim S., Schwarzbauer J., Kronimus A., Littke R., Woda C., Mangini A. (2004). Geochronology ofanthropogenic pollutants in riparian wetland sediments of the Lippe River(Germany). Org. Geochem. 35. 409–25.

Hii Y. S., Law A. T., Shazili N. A. M., Abdul-Rashid M. K., Lee C. W. (2009). Biodegradation of Tapis blended crude oil in marine sediment by a consortium of symbiotic bacteria. Inter. Biodet. Biodeg. 63.142–50.

Holt E., Audy O., Booij P., Melymuk L., Klánová J. (2017). Organochlorine pesticides in the indoor air of a theatre and museum in the Czech Republic: Inhalation exposure and cancer risk. Sci. of The Tot. Environ. Vol. 609. 598-606.

Holt M. S., Bernstein S. L. (1992). Linear alkylbenzenes in sewage sludges and sludge amended soils. Water Research. Vol. 26., Issue 5, May 1992, Pages 613-624.

Hosokawa Y., Yasui M., Yoshikawa K., Tanaka Y., Suzuki M. (2003). The nationwide investigation of endocrine disruptors in sediment of harbours. Mar. Poll. Bull.47, 132-138.

Hong W., Jia H., Li Y., Sun Y., Wang L. (2016). Polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs in the coastal seawater, surface sediment and oyster from Dalian, Northeast China. Ecotoxicol. Environ. Safe. Vol. 128. 11-20.

HSDB (2003) Hexachlorocyclohexanes. Environmental standards and regulations. Hazardous Substances Data Bank, Bethesda, MD.

HSDB (2007) Heptachlor. Environmental standards and regulations. Hazardous Substances Data Bank, Bethesda, MD

Hu Y., Li G., Yan M., Ping C., Ren J. (2014). Investigation into the distribution of polycyclic aromatic hydrocarbons (PAHs) in wastewater sewage sludge and its resulting pyrolysis bio-oils. Sci. Tot. Environ. Vol. 473–474. 459-464.

Huang S. L., Tuan N. N., Lee K. (2016). Occurrence, Human Intake and Biodegradation of Estrogen-Like Nonylphenols and Octylphenols. Curr. Drug. Metab. 17. 293-302.

Ibigbami O. A., Aiyesanmi A. F., Adeyeye E. I., Adebayo A. O., Aladesanwa R. D. (2015). Distribution, Bioconcentration and Potential Health Risks Associated with Organochlorine Pesticides Contamination of Chrysichthys nigrodigitatus and Oreochromis niloticus from Ero River in Nigeria. Journal of Chemical, Biological and Physical Sciences. JCBPS; Section D; August 2015 – October 2015, Vol. 5, No. 4; 4741-4751. E- ISSN: 2249 –1929.

Ieda T., Horii Y., Petrick G., Yamashita N., Ochiai N., Kannan K. (2005). Analysis of Nonylphenol Isomers in a Technical Mixture and in Water by Comprehensive Two-Dimensional Gas Chromatography-Mass Spectrometry: Environ. Sci. Tech. 39. 18. 7202-7207.

INERIS (2007): Regional action of search and reduction discharges of dangerous substances in water by the classified installations and the urban wastewater treatment plants (in French), INERIS, Verneuil-en-Halatte, Oise, France.

Inomata Y., Kajino M., Sato K., Ohara T., Kurokawa J., Ueda H., Tang N., Hayakawa K., Ohizumi T., Akimoto H. (2012). Emission and Atmospheric Transport of Particulate PAHs in Northeast Asia. Environ. Sci. Technol. 4941–4949.

International Programme on Chemical Safety IPCS (1998) Environnemental Health Criteria 202: selected non-heterocyclic polycyclic aromatic hydrocarbons. International Programme on Chemical Safety, World Health organization, Geneva, Switzerland.

Institut National de l'Environnement industriel et des Risques-INERIS (2006) Brignon J._M., Soleille S. Données technico-économiques sur les substances chimiques en France: les HAP. Brignon, J M. Soleille S.

International Agency for Research on Cancer IARC (1983) Monographs on the evaluation of the carcinogenic risk of chemicals to humans. Polynuclear aromatic compounds, Vol 32, Part 1, Chemical, environmental and experimental data, Lyon, France, p. 211-24

IPCS (International Programme On Chemical Safety). Polycyclic aromatic hydrocarbons, selected non-heterocyclic; 2010. http://www.inchem.org/documents/ehc/ehc/ ehc202.htm.

Ishiwatari R., Takada H., Yun S. J. A. (1983). Alkylbenzene pollution of Tokyo Bay sediments. Nature, 301, 599-600.

Isobe T., Nishiyama H., Nakashima A., Takada H. (2001). Distribution and behavior of nonylphenol, octylphenol, and nonylphenol monoethoxylate in Tokyo metropolitan area: their association with aquatic particles and sedimentary distributions. Environ. Sci. Technol. 35. 1041–1049.

Isobe K. O., Zakaria M. P., Chiem N. H., Minh L. Y., Prudente M., Boonyatumanond R. (2004). Distribution of linear alkylbenzenes (LABs) in riverine and coastal environments in South and Southeast Asia. Water. Res. 38. 2449–59.

Ismail N. A. H., Wee S. Y., Aris A. Z. (2018). Bisphenol A and alkylphenols concentrations in selected mariculture fish species from Pulau Kukup, Johor, Malaysia. Mar. Poll. Bull. Vol. 127. 536-540.

IUCLID. (1994). Dataset, nitrofen, CAS 1836-75-5, 18.2.2000.

Iwata H., Tanabe S., Aramoto M., Sakai N., Tatsukawa R. (1994). Persistent organochlorine residues in sediments from the Chukchi Sea, Bering Sea and Gulf of Alaska. Mar. Pollut. Bullet. Vol. 28. 746-753.

James R. R., Xu J. (2012). Mechanisms by which pesticides affect insect immunity. Journal of Invertebr. Patholog. Vol. 109. 2. 175-182.

Jafarabadi A. R., Bakhtiari A. R., Aliabadian M., Laetitia H., Yap. (2018). First report of bioaccumulation and bioconcentration of aliphatic hydrocarbons (AHs) and persistent organic pollutants (PAHs, PCBs and PCNs) and their effects on alcyonacea and scleractinian corals and their endosymbiotic algae from the Persian Gulf, Iran: Inter and intra-species differences. Sci. Tot. Environ. Vol. 627. 141-157.

Janicki T., Krupiński M., Długoński J. (2016). Degradation and toxicity reduction of the endocrine disruptors nonylphenol, 4-tert-octylphenol and 4-cumylphenol by the non-ligninolytic fungus Umbelopsis isabellina. Biores. Tech. Vol. 200. 223-229.

Jeon S., Hong S., Kwon B., Park J, Khim J .S. (2017). Assessment of potential biological activities and distributions of endocrine-disrupting chemicals in sediments of the west coast of South Korea. Chem. Vol. 168. 441-449.

Jernelöv A. 2018. Environmental Effects of Terrestrial Oil Spills. Encycl. Anthrop. Vol. 1. 323-335.

Jiménez-Díaz I., Ballesteros O., Zafra-Gómez A., Crovetto G., Vílchez J L., Navalón A., de Verge C., Ferrer J. A. (2010). New sample treatment for the determination of alkylphenols and alkylphenol ethoxylates in agricultural soils. Chem. 248-55.

Johnson A. C., White C., Bhardwaj L., Jurgens M. D. (2000). Potential for octylphenol to biodegrade in some English rivers. Environ. Toxicol. Chem. 19. 2486–92.

Junqué E., Garí M., Llull R M., Grimalt J.O. (2018). Drivers of the accumulation of mercury and organochlorine pollutants in Mediterranean lean fish and dietary significance. Sci. Tot. Environ. Vol. 634. 170-180.

Jurado E., Zaldívar J., Marinov D., Dachs J. (2007). Fate of persistent organic pollutants in the water column: Does turbulent mixing matter ?. Mar. Poll. Bull. Vol. 54. 441-451.

Kampire E., Rubidge G., Adams J. B. (2015). Distribution of polychlorinated biphenyl residues in sediments and blue mussels (Mytilus galloprovincialis) from Port Elizabeth Harbour, South Africa. Mar. Poll.Bull. Vol. 91. 173-179.

Kadi M. W., Ali N., Albar H. M. S. A. (2018). Phthalates and polycyclic aromatic hydrocarbons (PAHs) in the indoor settled carpet dust of mosques, health risk assessment for public. Sci. Tot. Environ. Vol. 627. 134-140.

Kameda T. (2011). Atmospheric Chemistry of Polycyclic Aromatic Hydrocarbons and Related Compounds. Vol. 57. 504-511.

Kaminski N. E., Kaplan B. L. F., Holapple M. P. (2008). Toxic responses of the immune system. In: Klaassen CD (ed) Casarett and Doull's Toxicology – The Basic Sci. of Pois. 7th ed., in: Curtis D. vol. 526.

Kang J. H., Kondo F., Katayama Y. (2006b). Human exposure to bisphenol A. Toxicology 226, 79–89

Kanzari F., Syakti A. D., Asia L., Malleret L., Mille G., Jamoussi B., Abderrabba M., Doumenq P. (2012) Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine, and organophosphorous pesticides in surface sediments from the Arc river and the Berre lagoon, France. Environmental science and pollution research international 19 : 559-576

Kaya D., Imamoglu I., Sanin F D., Sowers K. R. (2018). A comparative evaluation of anaerobic dechlorination of PCB-118 and Aroclor 1254 in sediment microcosms from three PCB-impacted environments. J. Hazard. Mat. Vol. 341. 328-335.

Kalliora Ch., Mamoulakis Ch., Vasilopoulos E., Stamatiades G A., Tsatsakis A. (2018). Association of pesticide exposure with human congenital abnormalities. Toxicol. and Appl. Pharmacol. Vol. 346. 58-75.

Ke C. L., Gu Y.G., Liu Q., Li L., Sun Z. (2017). Polycyclic aromatic hydrocarbons (PAHs) in wild marine organisms from South China Sea: Occurrence, sources, and human health implications. Mar. Pollut. Bullet. Vol. 117. 507-511.

Keita M., Nicolle A., El Bakali A. (2016). A wide range kinetic modeling study of PAH formation from liquid transportation fuels combustion. Combust. Flam. Vol. 174. 50-67.

Keshavarzifard K., Moore F., Keshavarzi B., Sharifi R. (2017). Polycyclic aromatic hydrocarbons (PAHs) in sediment and sea urchin (Echinometra mathaei) from the intertidal ecosystem of the northern Persian Gulf: Distribution, sources, and bioavailability. Mar.Poll. Bull. Vol.123. 373-380.

Khatib H. (2014). Oil and natural gas prospects: Middle East and North Africa. Energy Policy, Volume 64.71-77

Khetan S. K., Collins T. J. (2007). Human pharmaceuticals in the aquatic environment: a challenge to green chemistry. Chem Rev 107 : 2319 - 64.

Kilunga P. I., Sivalingam P., Laffite A., Grandjean D., Poté J. (2017). Accumulation of toxic metals and organic micro-pollutants in sediments from tropical urban rivers, Kinshasa, Democratic Republic of the Congo. Chem. Vol. 179. 37-48.

Knerr S., Schrenk D. (2006). Carcinogenicity of "non-dioxinlike" polychlorinated biphenyls Crit. Rev. Toxicol., 36 (2006), pp. 663-694

Koba O., Grabicova K., Cerveny D., Turek J., Kolarova J., Randak T., Zlabek V., Grabic R. (2018). Transport of pharmaceuticals and their metabolites between water and sediments as a further potential exposure for aquatic organisms. J. Hazard. Mat. 342. 401–407.

Kolpin D. W., Furlong E. T., Meyer M. T., Thurman E. M., Zaugg S D., Barber L. B. (2002). Pharmaceuticals, hormones and other organic wastewater contaminants in US streams,1999 2000: a national reconnaissance. Environ. Sci. Technol. 2002;36:1202 – 11.

Klosterhaus S. L., Grace R., Hamilton C., Yee D., (2013). Method validation and reconnaissance of pharmaceuticals, personal care products,and alkylphenols in surface waters, sediments, and mussels in an urban estuary. Environ. Inter. 54. 92 – 99.

Kuan C., De Grandi-Hoffman G., Curry R J., Garber K V., Purucker S. T. (2018). Sensitivity analyses for simulating pesticide impacts on honey bee colonies. Ecol Model, Vol. 376. 15-27.

Kumar S., Kaushik G., Dar M. A., Nimesh S., Villareal-Chiu J. F. (2018). Microbial Degradation of Organophosphate Pesticides : A Review Pedosp. Vol. 28.190-208.

Kumar S., Sajwan K. S., Richardson J P., Kannan K. (2008). Contamination profiles of heavy metals, organochlorine pesticides, polycyclic aromatic hydrocarbons and alkylphenols in sediment and oyster collected from marsh/estuarine Savannah GA, USA. Mar Pollut Bull. 56. 136-49.

Kurihara R., Watanabe E., Ueda Y., Kakuno A., Fujii K., Shiraishi F., Hashimoto S. (2007). Estrogenic activity in sediments contaminated by nonylphenol in Tokyo Bay (Japan) evaluated by vitellogenin induction in male mummichogs (Fundulus heteroclitus). Mar. Pollut. Bull. 54. 1315-1320.

Kuzu S. L., Saral A., Güneş G., Karadeniz A. (2016). Evaluation of background soil and air polychlorinated biphenyl (PCB) concentrations on a hill at the outskirts of a metropolitan city. Chem. Vol. 154. 79-89.

Kuo C. Y., Chien P.S., Kuo W.C., Wei C.T., Rau J.Y. (2012). Comparison of polycyclic aromatic hydrocarbon emissions on gasoline- and diesel-dominated routes. Environ Monit. Assess, 185. 5749-5761.

Lamparczyk H., Ochocka R.J., Gryzbowski J., Halkiewicz J., Radecki A. (1988) Parameters related to pollution by n-alkanes and PAH in Baltic water and sediments. Marine pollution bulletin 19(5), 222-226.

Laborie S., Moreau-Guigon E., Alliot F., Desportes A., Oziol L., Chevreuil M. (2016). A new analytical protocol for the determination of 62 endocrine-disrupting compounds in indoor air. Talanta. 147.132-41.

Langford K. H., Scrimshaw M. D., Birkett J. W., Lester J. N. (2005). Degradation of nonylphenolic surfactants in activated sludge batch tests. Water Res. 39 (5) : 870-6.

Lai I. C., Lee C.L., Zeng K.Y., Huang H.C. (2011). Seasonal variation of atmospheric polycyclic aromatic hydrocarbons along the Kaohsiung coast, J Environ. Manage. 92. 2029–2037.

Lauby-Secretan B., Loomis D., Grosse Y., El Ghissassi F., Bouvard V., Benbrahim-Tallaa L., Guha N., Baan R., Mattock H., Straif K. (2013). On behalf of the International Agency for Research on Cancer Monograph Working Group IARC, Lyon, France. Carcinogenicity of polychlorinated biphenyls and polybrominated biphenyls Lancet Oncol., 14. 287-288.

Lee C., Lee B., Keun C W., Hong S., Khim J. (2014). Environmental and ecological effects of Lake Shihwa reclamation project in South Korea: A review. Ocean & Coastal Management, Vol.102. Part B. 545-558.

Li J., Dong H., Xu X., Han B., Zhang D. (2016). Prediction of the bioaccumulation of PAHs in surface sediments of Bohai Sea, China and quantitative assessment of the related toxicity and health risk to humans. Mar. Poll. Bull. Vol. 104. 92-100.

Li Y., Niu J., Shen Z., Zhang C., Wang Z., He T. (2014) Spatial and seasonal distribution of organochlorine pesticides in the sediments of the Yangtze Estuary. Chemosphere 114, 233-240.

Li D., Kim M., Shim W. J., Yim U. H., Oh J. R., Kwon Y. J. (2004). Seasonal flux of nonylphenol in Han River, Korea.Chem. 56. 1-6.

Li X., Li P., Yan L., Chen J., Cheng T., Xu S. (2011). Characterization of polycyclic aromatic hydrocarbons in fog–rain events. J Environ Monit. 3. 2988–2993

Lima M.B., Feitosa E.A., Emídio E.S., Dórea H.S., Alexandre M.R. (2012) Distribution and sources of aliphatic hydrocarbons in surface sediments of Sergipe River estuarine system. Marine pollution bulletin 64(8), 1721-1725.

Liu D., Liu J., Guo M., Xu H., Zhang S., Shi L., Yao C. (2016) Occurrence, distribution, and risk assessment of alkylphenols, bisphenol A, and tetrabromobisphenol A in surface water, suspended particulate matter, and sediment in Taihu Lake and its tributaries. Marine pollution bulletin 112(1), 142-150.

Liu L., Liu Y., Lin J., Tang N., Hayakawa K., Maeda T. (2007) Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: A review. Journal of Environmental Sciences 19(1), 1-11.

Liu R., Zhang Y., Ding R., Li D., Gao Y., Yang M. (2009). Comparison of archaea and bacterial community structures in heavily oil-contaminated and pristine soils. J. Biosci. Bioengin. 108. 400–7.

Li G., Lang Y., Gao M., Yang W., Wang X. (2014). Carcinogenic and mutagenic potencies for different PAHs sources in coastal sediments of Shandong Peninsula. Mar. Poll. Bull. Vol. 84. 418-423.

Liu T., Guo Y., Peng N., Lang Q., Liu Z. (2018). Identification and quantification of polycyclic aromatic hydrocarbons generated during pyrolysis of sewage sludge: Effect of hydrothermal carbonization pretreatment. J. Anal. Appl. Pyrol.Vol. 130. 99-105.

Li-bin L., Yan L., Jin-ming L., Ning T., Kazuichi H., Tsuneaki M. (2016). Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: A review. Environ Sci Pollut Res Int. 23: 11598–11610.

List of Undesirable Substances (LOUS) (2009). Denish Ministery of the Environment. Environmental Protection Agency. Environmental Review No. 3. 2011 Orientering fra Miljøstyrelsen.

Liu L., Tang J., Zhong G., Zhen X., Tian C. (2018). Spatial distribution and seasonal variation of four current-use pesticides (CUPs) in air and surface water of the Bohai Sea, China. Sci. of The Tot. Environ. Vol. 621. 516-523.

Li Y., Niu J., Shen Z., Zhang C., Wang Z., He T. (2014). Spatial and seasonal distribution of organochlorine pesticides in the sediments of the Yangtze Estuary. Chem. Vol. 114. 233-240.

Li Y., Duan X., Li X., Zhang D. (2013a). Photodegradation of nonylphenol by simulated sunlight. Mar. Pollut. Bull. 66, 47–52.

Lin T., Li J., Xu Y., Liu X., Zhang G. (2012). Organochlorine pesticides in seawater and the surrounding atmosphere of the marginal seas of China: Spatial distribution, sources and air–water exchange. Sci. of The Tot. Environ. Vol. 435–436. 244-252.

Lin J.G., Chen Sh. Y. (1997). The relationship between adsorption of heavy metal and organic matter in river sediments. Environ. Intern. Vol. 24. No. 3, pp. 345-352, 1998.

Liu L., Tang J., Zhong G., Zhen X., Tian C. (2018). Spatial distribution and seasonal variation of four current-use pesticides (CUPs) in air and surface water of the Bohai Sea, China. Sci. of The Tot. Environ. Vol. 621. 516-523.

Liu D., Liu J., Guo M., Zhou H., Xu S., Zhang L., Shib L., Cheng Y. (2016). Occurrence, distribution, and risk assessment of alkylphenols, bisphenol A, and tetrabromobisphenol A in surface water, suspended particulate matter, and sediment in Taihu Lake and its tributaries. Mar. Poll. Bull. Vol. 112. 142-150.

Llorca-Porcel J., Martínez-Sánchez G. Álvarez B., Cobollo M. A., Valor I. (2009). Analysis of nine polybrominated diphenyl ethers in water samples by means of stir bar sorptive extraction-thermal desorption-gas chromatography–mass spectrometry. Analytica Chimica Acta Vol. 569. 113-118.

Lorenc J. L., Scheffer G. (2003). Alkylphenols. In: Kirk Othmer encyclopedia of chemical technology. Wiley, New York.

Lu J., Jin Q., He Y., Wu J., Zhang W., Zhao J. (2008). Biodegradation of nonylphenol polyethoxylates by denitrifying activated sludge. Wat. Res. Vol. 42.

Lu J., Zhao S. (2015). China's natural gas exploration and development strategies under the new normal. Natural Gas Industry B, Vol. 2. 473-480.

Lu X., Chen M., Zhang X., Sun Y., Zhu D., Zhang Q., Wang B., Zhang Z. (2016). Simultaneous quantification of five phenols in settled house dust using ultra-high performance liquid chromatography-tandem mass spectrometry Anal. Meth., 5.5339-5344.

Lu Q., Futter M. N., Nizzetto L., Bussi M. D. J., Whitehead P. G. (2016). Fate and transport of polychlorinated biphenyls (PCBs) in the River Thames catchment - Insights from a coupled multimedia fate and hydrobiogeochemical transport model. Sci Total Environ. 1. 572.1461-1470.

Luellen D.R., Shea D. (2002) Calibration and Field Verification of Semipermeable Membrane Devices for Measuring Polycyclic Aromatic Hydrocarbons in Water. Environmental Science & Technology 36(8), 1791-1797.

Luo X. J., Chen S. J., Ni H. G., Yu M., Mai B X. (2008).Tracing sewage pollution in the Pearl River Delta and its adjacent coastal area of South China Sea using linearalkylbenzenes (LABs). Mar. Pollut. Bull. 56. 158–162.

Luzardo O. P., Ruiz-Suárez N., Henríquez-Hernández L. A., Valerón P. F., Boada L. D. (2014). Assessment of the exposure to organochlorine pesticides, PCBs and PAHs in six species of predatory birds of the Canary Islands, Spain. Sci.Tot. Environ. Vol. 472.146-153.

Lyons B., Barber J., Rumney, H., Bolam, T., Bersuder, P., Law, R., Mason, C., Smith, A., Morris, S. and Devlin, M. (2015) Baseline survey of marine sediments collected from the State of Kuwait: PAHs, PCBs, brominated flame retardants and metal contamination. Marine pollution bulletin 100(2), 629-636.

Lyng N. L., Clausen C., Lundsgaard H., Andersen V. (2016). Modelling the impact of room temperature on concentrations of polychlorinated biphenyls (PCBs) in indoor air. Chem. Vol. 144. 2127-2133.

Macıas-Zamora J., Mendoza-Vega E., Villaescusa-Celaya J. (2002). PAHs composition of surface marine sediments: a comparison to potential local sources in Todos Santos Bay, BC, Mexico. Chemosphere 46(3), 459-468.

Mahjoubi M., Jaouani A, Guesmi A., Ben Amor S., Jouini A., Cherif H., Najjari A., Boudabous A., Koubaa N., Cherif A. (2013). Hydrocarbonoclastic bacteria isolated from petroleum contaminated sites in Tunisia: isolation, identification and characterization of the biotechnological potential. New Biotec.Vol. 30. 723-733.

Marchand C., Fernandez J. M., Moreton B., Landi L., Baltzer F. (2012). The partitioning of transitional metals (Fe, Mn, Ni, Cr) in mangrove sediments downstream of a ferralitized ultramafic watershed (New Caledonia). Chem. Geo.Vol. 300–301.70-80.

Maguire R. J. (1999). Review of the persistence of nonylphenol and nonylphenol ethoxylates in aquatic environments. Water Qual. Res. J. Can. 34, 37–78.

Ma W., Liu L., Jia H., Yang M., Li Y. (2018). PAHs in Chinese atmosphere Part I: Concentration, source and temperature dependence. Atmosph. Environ. Vol. 173. 330-337.

Masih J., Masih A., Kulshrestha A., Singhvi R., Taneja A. (2010). Characteristics of polycyclic aromatic hydrocarbons in indoor and outdoor atmosphere in the North central part of India. J Hazard Mater. 177 : 190–198.

Malarut J., Vangnai K. (2018). Influence of wood types on quality and carcinogenic polycyclic aromatic hydrocarbons (PAHs) of smoked sausages. Food Control, Vol. 85. 98-106.

Machala M., Bláha L., Vondráček J., Trosko J.E., Scott B.L. (2003). Upham Inhibition of gap junctional intercellular communication by noncoplanar polychlorinated biphenyls: inhibitory potencies and screening for potential mode(s) of action Toxicol. Sci., 76. 102-111

Magnusson K., Tiselius P. (2010). The importance of uptake from food for the bioaccumulation of PCB and PBDE in the marine planktonic copepod Acartia clause. Article in Aquatic toxicology (Amsterdam, Netherlands) 98 (4) : 374-80.

Wlodarczyk – Makula M. (2012). Half-Life of carcinogenic polycyclic aromatic hydrocarbons in stored sewage sludge. Department of Environmental Chemistry, Water and Wastewater Technology Częstochowa University of Technology Archive of environmental protection Vol. 38 No 32 pp 33 – 34. 2012.

Markey C. M., Michaelson C. L., Sonnenschein C., Sot A. M. (2001). Alkylphenols and Bisphenol A as Environmental Estrogens. The Handbook of Environmental Chemistry Vol. 3, Part Endocrine Disruptors, Part I.

Marcomini A., Pavoni B., Donazzolo R., Orio A. A. (1986). Combined preparative and analytical use of normal phase and reversed-phase high-performance liquid chromatography for the determination of aliphatic and polycyclic aromatic hydrocarbons in sediments of the Adriatic sea. Marine Chemistry, 18, 71-84.

Marcomini A., Stelluto S., Pavoni B. (1989). Determination of Linear Alkylbenzenesulphonates and Alkylphenol Polyethoxylates in Commercial Products and Marine Waters by Reversed- and Normal-Phase HPLC. 207-218. https://doi.org/10.1080/03067318908028395 .

Marr G. A., Lawson R. J., Chan S. F. (2000). Recent innovation in LAB process technology, 5th Cesio World Surfactants Congress V.1: 138-146, May-June, Firenze, Italy.

Martyniuk C. J., Doperalski N. J., Feswick A., Prucha M. S., Denslow N. D. (2016). Transcriptional networks associated with the immune system are disrupted by organochlorine pesticides in largemouth bass (Micropterus salmoides) ovary. Aqua. Toxicol. Vol. 177. 405-416.

Masih J., Singhvi R., Kumar K., Jain V.K., Taneja A.. (2012). Seasonal variation and sources of PAHs in indoor and outdoor air in a semi arid truct of northern India. Aerosol Air Qual Res 12 (2012) 515–525

Masih A., Taneja A. (2006). Polycyclic aromatic hydrocarbons (PAHs) concentrations and related carcinogenic potencies in soil at a semi-arid region of India. Chemosphere 65, 449–456.

Masood N., Zakaria M P., Halimoon N., Aris A. Z., Magama S. M., Kannan N., Mustafa S., Mohd Ali M., Keshavarzifard M., Vaezzadeh V., Alkhadher S. A. A., Al-Odaini N. A. (2016). Anthropogenic waste indicators (AWIs), particularly PAHs and LABs, in Malaysian sediments: Application of aquatic environment for identifying anthropogenic pollution. Mar. Poll. Bull. 102.160–175.

Masri S. L., Li A., Dang J. H., Wu C. J. (2006). Source characterization and exposure modeling of gas-phase polycyclic aromatic hydrocarbon (PAH) concentrations in Southern California. Atmosph. Environ. Vol. 177. 175-186.

McConnell H. M., Gartrell B.D., Chilvers B.L., Finlayson S.T., Morgan K.J. (2015). Baseline hydrocarbon levels in New Zealand coastal and marine avifauna. Mar. Pollut. Bullet. Vol. 94. 290-298.

Meade L. E., Riva M., Blomberg M. Z., Brock A. K., Kautzman K. E. (2016). Seasonal variations of fine particulate organosulfates derived from biogenic and anthropogenic hydrocarbons in the mid-Atlantic United States. Atmo. Environ. Vol. 145. 405-414.

Médail F., Quézel P. (1997). Hot-Spots analysis for conservation of plant biodiversity in the Mediterranean Basin. Annales of the Missouri Botanique Garden, 84 : 112-127.

Medeiros P. M., Bıcego M. C. (2004). Investigation of natural and anthropogenic hydrocarbon inputs in sediments using geochemical markers. I. Santos, SP—Brazil. Mar. Poll. Bull. 49. 761–769.

Medeiros P. M., Bícego M. C., Castelao R. M., Del Rosso C., Fillmann G., Zamboni A. J. (2005). Natural and anthrophogenic hydrocarbons inputs to sediments of Patos Lagoon Estuary, Brazil. Environ Int 31: 77–87.

Melymuk L, Bohlin-Nizzetto P., Kukučka P., Vojta Š., Klánová J. (2016). Seasonality and indoor/outdoor relationships of flame retardants and PCBs in residential air. Environ. Poll. Vol. 218. 392-401.

Mezcua M, Martínez-Uroz M. A., Gómez-Ramos M. M., Gómez M. J., Fernández-Alba A. R. (2012). Analysis of synthetic endocrine-disrupting chemicals in food: A review . Talanta. Vol. 100. 90-106.

Monaco D., Chianese E., Riccio A., Delgado-Sanchez A., Lacorte S. (2017) Spatial distribution of heavy hydrocarbons, PAHs and metals in polluted areas. The case of “Galicia”, Spain. Marine pollution bulletin 121(1-2), 230-237.

Montone R. C., Martins C. C., Bícego M. C., Taniguchi S., da Silva D. A. M., Campos L. S., Weber. R. R. (2010). Distribution of sewage input in marine sediments around a maritime Antarctic research station indicated by molecular geochemical indicators. Sci. Tot. Environ. 408. 4665–4671

Mostafa A.R., Wade T.L., Sweet S.T., Al-Alimi A.K.A., Barakat A.O. (2009) Distribution and characteristics of polycyclic aromatic hydrocarbons (PAHs) in sediments of Hadhramout coastal area, Gulf of Aden, Yemen. Journal of Marine Systems 78(1), 1-8.

Moeder M., Martin C., Schlosser D., Harynuk J., Górecki T. (2006). Separation of technical 4-nonylphenols and their biodegradation products by comprehensive two-dimensional gas chromatography coupled to time-of-oflight mass spectrometry. J. Chrom. A, 1107, 233-239.

Moreira L. B., Castro Í. B., Hortellani M. A., Sasakie S. T., Mônica S. T., Pettie A. V., Jorge G. F., Bícego M. C., Costa-Lotufo L. V., Abessa D. M. S. (2017). Effects of harbor activities on sediment quality in a semi-arid region in Brazil. Ecotoxicol. Environ. Safe. Vol. 135. 137-151.

Moreau-Guigon E., Chevreuil M. (2014). Human exposure to endocrine disruptors via ambient air: An unknown health risk. Sci. Univ. Earth Sci. Geochem. 75 (1), pp.74-81.

Mortazavi S., Alireza R., Abbas B., Sari E., Bahramifar N., Rahbarizadeh F. (2013). Occurrence of Endocrine Disruption Chemicals (Bisphenol A, 4-Nonylphenol, and Octylphenol) in Muscle and Liver of, Cyprinus Carpino Common, from Anzali Wetland, Iran. Bull. Environ. Contam. Toxicol. 2013. 90:578–584

Monaco D., Chianese E., Riccio A., Delgado-Sanchez A., Lacorte S. (2017). Spatial distribution of heavy hydrocarbons, PAHs and metals in polluted areas. The case of “Galicia”, Spain. Mar. Pollut. Bullet. Vol. 121. 230-237.

Montgomery-Brown J., Drewes J E., Fox P., Reinhard M. (2003). Behavior of alkylphenol polyethoxylate metabolites during soil aquifer treatment. W. Res. Vol. 37. 3672-3681.

Mohanraj R., Dhanakumar S., Solaraj G. (2012). Polycyclic Aromatic Hydrocarbons Bound to PM 2.5 in Urban Coimbatore, India with Emphasis on Source Apportionment. Sci. World J. 980843.

Murillo W.A., Vieth-Hillebrand A., Horsfield B., Wilkes H. (2016) Petroleum source, maturity, alteration and mixing in the southwestern Barents Sea: New insights from geochemical and isotope data. Marine and Petroleum Geology 70, 119-143.

Murray A. P., Richardson B. J., Gibbs. C. F. (1991). Bioconcentration Factors for Petroleum Hydrocarbons, PAHs, LABs and Biogenic Hydrocarbons in the Blue Mussel. Vol. 2.2 Pergamon Press. Bureau of Mineral Resources, Geology and Geophysics.

Munaron D., Nathalie T., Budzinski H., Bruno A., Jean-Louis G. (2012). Pharmaceuticals, alkylphenols and pesticides in Mediterranean coastal waters: Results from a pilot survey using passive samplers. Estuar. Coast. Shelf Sci. 114. 82-92.

Muniz D. A., da Silva M., Bícego., Bromberg S., Pires-Vaninc A. M. S. (2015). Sewage contamination in a tropical coastal area (São Sebastião Channel, SP, Brazil) Mar. Poll.Bull.Vol. 99. 292-300.

Nam J. J, Sweetman A. J., Jones K. C. (2009). Polynuclear aromatic hydrocarbons (PAHs) in global background soils. J Environ Monit. 11: 45 – 8.

Naes K., Knutzen J., Berglind L. (1995). Occurrence of PAH in marine organisms and sediments from smelter discharge in Norway. Science of The Total Environment 163(1-3), 93-106.

Nakata H., Hirakawa Y., Kawazoe V., Nakabo T., Ding X. (2005). Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai city region, China. Environ. Poll. Vol. 133. 415-429.

Nascimento R. A., Almeida M., Escobar N. C. F, Ferreira S. L.C., Queiroz A. F. S. (2017). Sources and distribution of polycyclic aromatic hydrocarbons (PAHs) and organic matter in surface sediments of an estuary under petroleum activity influence, Todos os Santos Bay, Brazil. Mar. Poll. Bullet. Vol. 119. 223-230.

Nawab A., Aleem A., Malik A. (2003). Determination of organochlorine pesticides in agricultural soil with special reference to γ-HCH degradation by Pseudomonas strains. Biores. Tech. Vol. 88. 41-46.

Naifar I., Pereira F., Zmemla,R., Bouaziz M., Elleuch B., Garcia D. (2018) Spatial distribution and contamination assessment of heavy metals in marine sediments of the southern coast of Sfax, Gabes Gulf, Tunisia. Marine pollution bulletin 131, 53-62.

Ngô C., Régent A. (2012) Déchets, effluents et pollution-3e éd.: Impact sur l'environnement et la santé, Dunod.

Neal M. S., Zhu J., Foster W. G. (2008). Quantification of benzo[a]pyrene and other PAHs in the serum and follicular fluid of smokers versus non-smokers. Repro. Toxicol. Vol. 25. 100-106.

Nilsson E. D., Rannik Ü., Kumala M., Buzorius G., O’dowd C. D. (2001). Effects of continental boundary layer evolution, convection, turbulence and entrainment, on aerosol formation, Tellus B: Chemical and Physical Meteorology. 53. 4. 441-461.

Ni H. G., Lu F. H., Wang J. Z., Guan Y. F., Luo X. L., Zeng E.Y. (2008). Linear alkylbenzenes in riverine runoff of the Pearl River Delta (China) and their application as anthropogenic molecular markers in coastal environments. Environ. Pollut. 154 (2). 348–355.

Ni H G., Shen R. L., Zeng H., Zeng E. Y. (2009). Fate of linear alkylbenzenes and benzothiazoles of anthropogenic origin and their potential as environmental molecular markers in the Pearl River Delta, South China. Environ. Pollut. 157.3502–3507.

Noorimotlagh Z., Kazeminezhad I., Jaafarzadeh N., Ahmadi M., Martinez S. S. (2018). The visible-light photodegradation of nonylphenol in the presence of carbon-doped TiO2 with rutile/anatase ratio coated on GAC: Effect of parameters and degradation mechanism. J. Hazard. Mat. Vol. 350. 108-120.

Numata M., Yarita T., Aoyagi Y., Yamazaki M., Takatsu A. (2005). Investigation of saponification for determination of polychlorinated biphenyls in marine sediments. Chem. Vol. 58. 865-875.

Nzila A. (2018). Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons under anaerobic conditions: Overview of studies, proposed pathways and future perspectives. Environ. Poll. Vol. 239. pp 788-802.

Ohura T., Horii Y., Yamashita N. (2018). Spatial distribution and exposure risks of ambient chlorinated polycyclic aromatic hydrocarbons in Tokyo Bay area and network approach to source impacts. Environ. Pollut. Vol. 232. 367-374.

Ojeda G., Patrícioa J., Navajas H., Comellas L., Alcañiz J. M, Ortizc O., Marks E., Sousa T. N. (2013). Effects of nonylphenols on soil microbial activity and water retention. Applied Soil Ecology Vol. 64. 77-83

Ojeda G., Patrício J., Navajas H., Comellas L., Alcaiz J M., Marks O E., Natal-da-Luz T., Sousa J P. (2013). Effects of nonylphenols on soil microbial activity and water retention. Applied Soil Ecology 64 (2013) 77–83.

Okay O. S., Karacık V., Başak S., Henkelmann B., Schramm K. W. (2009). PCB and PCDD/F in sediments and mussels of the Istanbul strait (Turkey). Chem. Vol. 76. Issue 2. 159-166.

Olah G.A., Molnár Á. (2003) Hydrocarbon chemistry, John Wiley & Sons.

Ortuño N., Conesa J.A., Moltó J., Font R. (2014). Pollutant emissions during pyrolysis and combustion of waste printed circuit boards, before and after metal removal, Sci. Total Environ. 499 C. 27–35.

OSPAR (2001) Nonylphenol/nonylphenolethoxylates. Hazardous substances series. OSPAR (convention for the protection of the marine environment of the north-east Atlantic), London

Oziolor E. M., Apell J. N., Winfield Z. C., Back J A., Matson C. W., (2018). Polychlorinated biphenyl (PCB) contamination in Galveston Bay, Texas: Comparing concentrations and profiles in sediments, passive samplers, and fish. Environ. Poll. Vol. 236. 609-618.

Ovesen J. L., Schnekenburger M., Puga A. (2011). Aryl hydrocarbon receptor ligands of widely different toxic equivalency factors induce similar histone marks in target gene chromatin Toxicol. Sci., 121. 123-131.

Padilla-Sánchez J. A., Plaza-Bolaños P., Romero-González R., Garrido-Frenich A., Vidal J. L. M. (2010). Application of a quick, easy, cheap, effective, rugged and safe-based method for the simultaneous extraction of chlorophenols, alkylphenols, nitrophenols and cresols in agricultural soils, analyzed by using gas chromatography-triple quadrupole-mass spectrometry/mass spectrometry. J Chromatogr A. 1217. 5724-31.

Pan J., Yang Y., Xu V., Chen D., Xi D. (2007). PCBs, PCNs and PBDEs in sediments and mussels from Qingdao coastal sea in the frame of current circulations and influence of sewage sludge. Chem. Vol. 66.1971-1982.

Papadakis E., Tsaboula A., Vryzas Z., Kotopoulou A., Papadopoulou-Mourkidou E. (2018). Pesticides in the rivers and streams of two river basins in northern Greece. Sci. of The Tot. Environ. Vol. 624. 732-743.

Pezzotti M. L. G., Turemis V., Sanchís V., Giardi V. (2018). Fast pesticide pre-screening in marine environment using a green microalgae-based optical bioassay. Mar. Poll. Bull. Vol. 129. 212-221.

Pernica M., Poloucká P., Seifertová M., Šimek Z. (2015). Determination of alkylphenols in water samples using liquid chromatography-tandem mass spectrometry after pre-column derivatization with dansyl chloride. J Chromatogr A. 141.49-56.

Pesce S., Margoum Ch., Rouard N., Foulquier A., Martin-Laurent F. (2013). Freshwater sediment pesticide biodegradation potential as an ecological indicator of microbial recovery following a decrease in chronic pesticide exposure: A case study with the herbicide diuron. Ecolog. Indic. Vol. 29. 18-25

Pessah L. N., Hansen L.G., Albertson T.E., Garner C.E., Ta T.A., Do Z., Kim K.H., Wong P.W. (2006). Structure-activity relationship for noncoplanar polychlorinated biphenyl congeners toward the ryanodine receptor-Ca2+ channel complex type 1 (RyR1). Chem. Res. Toxicol., 19. pp. 92-101

Petrović M., Barceló D. (2000). The stability of non-ionic surfactants and linear alkylbenzene sulfonates in a water matrix and on solid-phase extraction cartridges. Fresenius J Anal Chem. 368. 7. 676-83.

Perez-Umphrey A. A., Burns C. M. B., Stouffer P. C., Woltmann V., Taylor S. S. (2018). Polycyclic aromatic hydrocarbon exposure in seaside sparrows (Ammodramus maritimus) following the 2010 Deepwater Horizon oil spill. Sci. Tot. Environ. Vol. 630. 1086-1094.

Pereira W. E., Hostettler F. D., Cashman J. R., Nishioka R. S. (1994). Occurrence and distribution of organochlorine compounds in sediment and livers of striped bass (Morone saxatilis) from the San Francisco Bay-Delta Estuary. Mar. Pollut. Bullet. Vol. 28. 434-441.

Pei Y., Halbrook R S., Li H., You J. (2017). Homing pigeons as a biomonitor for atmospheric PAHs and PCBs in Guangzhou, a megacity in South China. Mar. Pollut. Bullet. Vol. 124. 1048-1054.

Pesarini P.P., de Souza R. G. S., Corrêa R. J., Nicodem D. E., de Lucas N. C. (2010). Asphaltene concentration and compositional alterations upon solar irradiation of petroleum. Journal of Photochemistry and Photobiology A: Chem. Vol. 214, Issue 1, pp 48-53.

Perez-Umphrey A.A., Burns C.M.B., Stouffer P.C., Woltmann S., Taylor S.S. (2018) Polycyclic aromatic hydrocarbon exposure in seaside sparrows (Ammodramus maritimus) following the 2010 Deepwater Horizon oil spill. Science of The Total Environment 630, 1086-1094.

Pie H. V., Heyes A., Mitchelmore C. L. (2015). Investigating the use of oil platform marine fouling invertebrates as monitors of oil exposure in the Northern Gulf of Mexico. Sci. Tot. Environ. Vol. 508. 553-565.

Placencia J A., Contreras S. (2018). Organochlorine pesticides in surface waters from Reloncaví Fjord and the inner sea of Chiloé (~39.5°S - 43°S), Chilean Patagonia. Mar. Poll. Bull. Vol. 126. 389-395.

Pokhrel B., Gong P., Wang X., Chen M., Wang C., Gao S. (2018a) Distribution, sources, and air–soil exchange of OCPs, PCBs and PAHs in urban soils of Nepal. Chemosphere 200, 532-541.

Pokhrel B., Gong P., Wang X., Wang C., Gao,S. (2018b) Polycyclic aromatic hydrocarbons in the urban atmosphere of Nepal: Distribution, sources, seasonal trends, and cancer risk. Science of The Total Environment 618, 1583-1590.

Pongpiachan S., Hattayanone M., Tipmanee D., Suttinun O., Hirunyatrakul P. (2018). Chemical characterization of polycyclic aromatic hydrocarbons (PAHs) in 2013 Rayong oil spill-affected coastal areas of Thailand. Environ. Poll. Vol. 233. 992-1002.

Polidoro B. A., Comeros-Raynal M. T., Cahill T., Clement C., (2017). Land-based sources of marine pollution: Pesticides, PAHs and phthalates in coastal stream water, and heavy metals in coastal stream sediments in American Samoa. Mar. Pollut. Bullet.Vol.116. 501-507.

Pojana G., Gomiero A., Jonkers N., Marcomini A. (2007). Natural and synthetic endocrine disrupting compounds (EDCs) in water, sediment and biota of a coastal lagoon. Environ. Inter. Vol. 33. 929-936.

Porte C., Albaigés J. (1993). Bioaccumulation Patterns of Hydrocarbons and Polychlorinated Biphenyls in Bivalves, Crustaceans, and Fishes. Department of Environmental Chemistry. Arch. Environ. Contam. Toxicol. 26, 273-281 (1993).

Priac A., Morin-Crini N., Druart C., Gavoille S., Bradu C., Lagarrigue C., Torri G., Winterton P., Crini G. (2017) Alkylphenol and alkylphenol polyethoxylates in water and wastewater: A review of options for their elimination. Arabian Journal of Chemistry 10, S3749-S3773.

Pruell R. J., Hoffman E. J., Quinn J.G. (1984) Total hydrocarbons, polycyclic aromatic hydrocarbons and synthetic organic compounds in the Hard shell clam, Mercenaria mercenaria, purchased at commercial seafood stores. Marine environmental research 11(3), 163-181.

Pretty J., Bharucha Z. P. (2015). Integrated Pest Management for Sustainable Intensification of Agriculture in Asia and Africa. Insects 2015, 6(1), 152-182.

Pu Y., Wang C., Meyers,P.A. (2017) Origins of biomarker aliphatic hydrocarbons in sediments of alpine Lake Ximencuo, China. Palaeogeography, Palaeoclimatology, Palaeoecology 475, 106-114.

Pućko M., Stern G A., Burt A. E., Jantunen L. M., Rysgaard S. (2017). Current use pesticide and legacy organochlorine pesticide dynamics at the ocean-sea ice-atmosphere interface in resolute passage, Canadian Arctic, during winter-summer transition. Sci. of The Tot. Environ. Vol. 580. 1460-1469.

Pu Y., Wang C., Meyers P. A. (2017). Origins of biomarker aliphatic hydrocarbons in sediments of alpine Lake Ximencuo, China. Palaeogeography, Palaeoclimatology, Palaeoecology, Vol. 475. 106-114.

Qamar Z., Khan S., Khan A., Aamir M., Waqas M. (2017). Appraisement, source apportionment and health risk of polycyclic aromatic hydrocarbons (PAHs) in vehicle-wash wastewater, Pakistan. Sci. Tot. Environ. Vol. 605–606. 106-113.

Qu C., Sun Y., Albanese S., Lima A., De Vivo B. (2017). Organochlorine pesticides in sediments from Gulfs of Naples and Salerno, Southern Italy. J. Geochem. Explor. In press, corrected proof, Available online 19 December 2017.

Rajendran R. K., Lin C., Huang V., R Kirschner. (2017). Enrichment, isolation, and biodegradation potential of long-branched chain alkylphenol degrading non-ligninolytic fungi from wastewater. Mar. Poll. Bull. Vol.125. 416-425.

Rajpara R. K., Dudhagara D. R., Bhatt J K., Gosai H. B, Dave B.P. (2017). Polycyclic aromatic hydrocarbons (PAHs) at the Gulf of Kutch, Gujarat, India: Occurrence, source apportionment, and toxicity of PAHs as an emerging issue. Mar. Poll. Bull. Vol. 119. 231-238.

Ramalho-Santos J., Tavares R S. (2018). Endocrine Disruptors and Male Reproductive Function. Ref. Mod. Biomed. Sci..

Ravindra K., Sokhi R.S., Van Grieken R. (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. In: Atmo. Environ.Vol. 42. 2895-2921.

Ramalho-Santos J., Tavares R.S., (2018) Encyclopedia of Reproduction (Second Edition). Skinner, M.K. (ed), pp. 629-633, Academic Press, Oxford.

Readman J., Mantoura R., Rhead M. (1987) A record of polycyclic aromatic hydrocarbon (PAH) pollution obtained from accreting sediments of the Tamar estuary, UK: evidence for non-equilibrium behaviour of PAH. Science of The Total Environment 66, 73-94.

Rehman M. Y. E., Kamal A., Taqi M. M., Malik R. N. (2017). Tracing biomarker of PAH-exposure and susceptibility factor (GSTM-polymorphism) among cancer patients in Pakistan. Chem. Vol. 384-390.

Renner R. (1997). European bans on surfactant trigger transatlantic debate. Environ. Sci. Technol. 31 : 316 A - 320 A.

Reid A. M., Brougham C. A., Fogarty A. M, Roche J J. (2008). Accelerated Solvent-Based Extraction and enrichment of Selected Plasticisers and 4-Nonylphenol, and extraction of tin from Organotin Sources in sediments, sludges and Leachate Soils. Anal. Chim. Acta. Vol. 634. pp. 197-204.

Ritter R. M., Scheringer M., MacLeod C., Moeckel K. C., Hungerbühler J K. (2011). Intrinsic Human Elimination Half-Lives of Polychlorinated Biphenyls Derived from the Temporal Evolution of Cross-Sectional Biomonitoring Data from the United Kingdom. Environ Health Perspect. 119(2): 225–231.

Rizzi J., Taniguchi S., Martins C. C. (2017). Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in sediments from an urban- and industrial-impacted subtropical estuary (Babitonga Bay, Brazil). Mar. Poll. Bull.Vol.119. 390-395.

Riccardi C., Di Filippo P., Pomata D., Di Basilio M., Spicaglia S., Buiarelli F. (2013). Identification of hydrocarbon sources in contaminated soils of three industrial areas. Sci. Total. Environ. Vol. 450–451. 13-21.

Rontani J.F., Bosser-Joulak F., Rambeloarisoa E., Bertrand J. C., Faure R. (1985). Analytical study of Asthart crude oil asphaltenes biodegradation. Chemosphere, Volume 14, Issue 9 pp 1413-1422

Rodríguez A. G. P., López M. I. R., Casillas T. Á. D., León J. A. A., Prusty A. K. (2017). Monitoring of organochlorine pesticides in blood of women with uterine cervix cancer. Environ. Pollut, Vol. 220. 853-862.

Ruiz-Guzmán J. A., Gómez-Corrales P., Cruz-Esquivel Á., Marrugo-Negrete J. L. (2017). Cytogenetic damage in peripheral blood lymphocytes of children exposed to pesticides in agricultural areas of the department of Cordoba, Colombia. Mutation Research/Genetic Toxicol. and Environ. Mutagen. Vol. 824. 25-31.

Rushdi A.I., Al-Mutlaq K., El-Mubarak A.H., El-Otaibi M. (2013) Occurrence and sources of aliphatic hydrocarbons in surface soils from Riyadh city, Saudi Arabia. Journal of the Saudi Society of Agricultural Sciences 12(1), 9-18.

Salgueiro-González N., Turnes-Carou I., Viñas-Diéguez L., Muniategui-Lorenzo S., Prada-Rodríguez D. (2015). Occurrence of endocrine disrupting compounds in five estuaries of the northwest coast of Spain: Ecological and human health impact. Chem.Vol.131. 241-247.

Saliot A., Tronczynski J., Scribe P., Letolle R. (1988). The application of isotopic and biogeochemical markers to the study of the biochemistry of organic matter in a macrotidal estuary, the Loire, France. Estuarine, Coastal and Shelf Science, Volume 27, Issue 6, December 1988, Pages 645-669.

Sarker S., Vashistha D., Sarker M S., Sarkar A. (2018). DNA damage in marine rock oyster (Saccostrea Cucullata) exposed to environmentally available PAHs and heavy metals along the Arabian Sea coast. Ecotoxicol. Environ. Safe. Vol. 151. 132-143.

Saija I., Mangano V., Casale K. E., La Torre G. L., Salvo A. (2016). Determination and quantification of PCBs, POCs and PAHs in Thunnus thynnus from the Straits of Messina (Italy). Data in Brief, Vol. 7.129-134

Sarigiannis D. A, Karakitsios S. P., Zikopoulos D., Nikolaki S., Kermenidou M. (2015). Lung cancer risk from PAHs. emitted from biomass combustion. Environ. Res. Vol.137. 147-156.

Saeed T., Al-Jandal N., Abusam A., Taqi H., Al-Khabbaz A., Zafar J. (2017). Sources and levels of endocrine disrupting compounds (EDCs) in Kuwait's coastal areas. Mar Pollut Bull. 118. 407-412.

Sadeu J. C., Foster W. G. (2013). The cigarette smoke constituent benzo[a]pyrene disrupts metabolic enzyme, and apoptosis pathway member gene expression in ovarian follicles. Repro. Toxicol. Vol. 40. 52-59.

Sakai M., Ezaki S., Suzuki N., Kurane R. (2005). Isolation and characterization of a novel polychlorinated biphenyl-degrading bacterium, Paenibacillus sp. KBC101, Appl. Microbiol. Biotechnol. 68.111–116.

Sánchez-Osorio J. L., Macías-Zamora J. V., Ramírez-Álvarez N., Bidleman T. F. (2017). Organochlorine pesticides in residential soils and sediments within two main agricultural areas of northwest Mexico: Concentrations, enantiomer compositions and potential sources. Chem. Vol. 173. 275-287.

Salapasidou M., Samara C., Voutsa D. (2011). Endocrine disrupting compounds in the atmosphere of the urban area of Thessaloniki, Greece. Atmos. Environ. Vol. 45. 3720-3729.

Saito I., Onuki A., Seto H. (2004). Indoor air pollution by alkylphenols in Tokyo. Indoor Air. 5. 325-32.

Sarigiannis D.A., Karakitsios S.P., Zikopoulos D., Nikolaki S., Kermenidou M. (2015) Lung cancer risk from PAHs emitted from biomass combustion. Environmental Research 137, 147-156.

Sarker S., Vashistha D., Sarker M.S., Sarkar A. (2018) DNA damage in marine rock oyster (Saccostrea Cucullata) exposed to environmentally available PAHs and heavy metals along the Arabian Sea coast. Ecotoxicology and Environmental Safety 151, 132-143.

Saija E., Mangano V., Casale K.E., La Torre G.L., Dugo G., Salvo A. (2016) Determination and quantification of PCBs, POCs and PAHs in Thunnus thynnus from the Straits of Messina (Italy). Data in brief 7, 129-134.

Salgueiro-González N., Turnes-Carou I., Viñas-Diéguez L., Muniategui-Lorenzo S., López-Mahía P., Prada-Rodríguez D. (2015) Occurrence of endocrine disrupting compounds in five estuaries of the northwest coast of Spain: ecological and human health impact. Chemosphere 131, 241-247.

Saeed T., Al-Muzaini S., Al-Bloushi A. (1996) Post-Gulf War assessment of the levels of PAHs in the sediments from Shuaiba Industrial Area, Kuwait. Water Science and Technology 34(7-8), 195-201.

Salgueiro-González N., Turnes-Carou I., Viñas-Diéguez L., Muniategui-Lorenzo S., Prada-Rodríguez D. (2015). Occurrence of endocrine disrupting compounds in five estuaries of the northwest coast of Spain: Ecological and human health impact. Chem.Vol.131. 241-247.

Saliot A., Tronczynski J., Scribe P., Letolle R. (1988). The application of isotopic and biogeochemical markers to the study of the biochemistry of organic matter in a macrotidal estuary, the Loire, France. Estuarine, Coastal and Shelf Science, Volume 27, Issue 6, December 1988, Pages 645-669.

Sarker S., Vashistha D., Sarker M S., Sarkar A. (2018). DNA damage in marine rock oyster (Saccostrea Cucullata) exposed to environmentally available PAHs and heavy metals along the Arabian Sea coast. Ecotoxicol. Environ. Safe. Vol. 151. 132-143.

Saija I., Mangano V., Casale K E., La Torre G. L., Salvo A. (2016). Determination and quantification of PCBs, POCs and PAHs in Thunnus thynnus from the Straits of Messina (Italy). Data in Brief, Vol. 7.129-134

Sarigiannis D. A., Karakitsios S. P., Zikopoulos D., Nikolaki S., Kermenidou M. (2015). Lung cancer risk from PAHs emitted from biomass combustion. Environ. Res. Vol.137. 147-156.

Saeed T., Al-Jandal N., Abusam A., Taqi H., Al-Khabbaz A., Zafar J. (2017). Sources and levels of endocrine disrupting compounds (EDCs) in Kuwait's coastal areas. Mar Pollut Bull. 118. 407-412.

Sadeu J. C., W G. Foster. (2013). The cigarette smoke constituent benzo[a]pyrene disrupts metabolic enzyme, and apoptosis pathway member gene expression in ovarian follicles. Repro. Toxicol. Vol. 40. 52-59.

Sakai M., Ezaki S., Suzuki N., Kurane R. (2005). Isolation and characterization of a novel polychlorinated biphenyl-degrading bacterium, Paenibacillus sp. KBC101, Appl. Microbiol. Biotechnol. 68.111–116.

Sánchez-Osorio J. L., Macías-Zamora J V., Ramírez-Álvarez N., Bidleman T. F. (2017). Organochlorine pesticides in residential soils and sediments within two main agricultural areas of northwest Mexico: Concentrations, enantiomer compositions and potential sources. Chem. Vol. 173. 275-287.

Salapasidou M., Samara C., Voutsa D. (2011). Endocrine disrupting compounds in the atmosphere of the urban area of Thessaloniki, Greece. Atmos. Environ. Vol. 45. 3720-3729.

Saito I., Onuki A., Seto H. (2004). Indoor air pollution by alkylphenols in Tokyo. Indoor Air. 5. 325-32.

Sarigiannis D.A., Karakitsios S.P., Zikopoulos D., Nikolaki S., Kermenidou M. (2015) Lung cancer risk from PAHs emitted from biomass combustion. Environmental Research 137, 147-156.

Sarker S., Vashistha D., Sarker M.S., Sarkar A. (2018) DNA damage in marine rock oyster (Saccostrea Cucullata) exposed to environmentally available PAHs and heavy metals along the Arabian Sea coast. Ecotoxicology and Environmental Safety 151, 132-143.

Saija E., Mangano V., Casale K.E., La Torre G.L., Dugo G., Salvo A. (2016) Determination and quantification of PCBs, POCs and PAHs in Thunnus thynnus from the Straits of Messina (Italy). Data in brief 7, 129-134.

Salgueiro-González N., Turnes-Carou I., Viñas-Diéguez L., Muniategui-Lorenzo S., López-Mahía P., Prada-Rodríguez D. (2015) Occurrence of endocrine disrupting compounds in five estuaries of the northwest coast of Spain: ecological and human health impact. Chemosphere 131, 241-247.

Saeed T., Al-Muzaini S., Al-Bloushi A. (1996) Post-Gulf War assessment of the levels of PAHs in the sediments from Shuaiba Industrial Area, Kuwait. Water Science and Technology 34(7-8), 195-201.

Scheringer M., Stroebe M., Wania F., Wegmann F., Hungerbuhler K. (2004). The effect of export to the deep sea on the long-range transport potential of persistent organic pollutants. Environ. Sci. Poll. Res. 11 (1), 41–48.

Schwarzenbach R. P., Gschwend P. M., Imboden D. M. (1993). Environmental organic chemistry, John Wiley and Sons, Inc, 1993

Schnelle-Kreis J., Sklorz M., Peters A., Zimmermann R. (2005). Analysis of Particle Associated Semi-Volatile Aromatic and Aliphatic Hydrocarbons in Urban Particulate Matter on a Daily Basis. Atmo. Environ. 39. 7702-7714

Schönkaes U. (1998) LAS, A modern classic surfactant, Chimica Oggi: 9-13.

Scheringer M., Stroebe M., Wania F., Wegmann F., Hungerbuhler K. (2004). The effect of export to the deep sea on the long-range transport potential of persistent organic pollutants. Environ. Sci. Poll. Res. 11 (1), 41–48.

Schwarzenbach R. P., Gschwend P M., Imboden D. M. (1993). Environmental organic chemistry, John Wiley and Sons, Inc, 1993

Schnelle-Kreis J., Sklorz M., Peters A., Zimmermann R. (2005). Analysis of Particle Associated Semi-Volatile Aromatic and Aliphatic Hydrocarbons in Urban Particulate Matter on a Daily Basis. Atmo. Environ. 39. 7702-7714

Schönkaes U. (1998). LAS, A modern classic surfactant, Chimica Oggi: 9-13.

Serrano A., Gallego M., González J.L., Tejada M. (2008) Natural attenuation of diesel aliphatic hydrocarbons in contaminated agricultural soil. Environmental Pollution 151(3), 494-502

Seto M., Ida M., Okita N., Hatta T., Masai E., Fukuda M. (1996). Catabolic potential of multiple PCB transformation systems in Rhodococcus sp. strain RHA1, Biotechnol. Lett. 18 (1996) 1305–1308.

Segment Forecasts To 2020. (2015). Linear Alkyl Benzene (LAB) Market Analysis By Application (Heavy Duty Laundry Liquids, Laundry Powders, Light Duty Dish Washing Liquids, Industrial Cleaners, Household Cleaners). P 85.

Serrazanetti G. P., Pagnucco C., Conte L.S., Artusi R. (1994). Aliphatic hydrocarbons and linear alkylbenzenes in zooplankton from the Gulf of Trieste. Chem.Vol. 28. 1119-1126.

Serrano A., Gallego M., González J. L., Tejada M. (2008). Natural attenuation of diesel aliphatic hydrocarbons in contaminated agricultural soil. Environ. Pollut.Vol.151.494-502.

Shabbir M., Singh M., Maiti S., Kumar S., Saha S K. (2018). Removal enactment of organo-phosphorous pesticide using bacteria isolated from domestic sewage. Biores.Tech. Vol. 263. 280-288

Sharma V. K., George A., Anquandah K., Yngard R A., Kim H., Fekete J., Bouzek K. (2009). Nonylphenol, octylphenol, and bisphenol-A in the aquatic environment: A review on occurrence, fate, and treatment. J. Environ. Sci. Health.Vol. 44. 423-442.

Shon H. K., Vigneswaran S., Cho J. (2008). Comparison of physico-chemical pretreatment methods to seawater reverse osmosis: Detailed analyses of molecular weight distribution of organic matter in initial stage. J. Memb. Sci. 320.151-158..

Shekhar S., Sood S., Showkat S., Lite C., Chandrasekhar A., Vairamani M., Barathi S., Santosh W. (2017) Detection of phenolic endocrine disrupting chemicals (EDCs) from maternal blood plasma and amniotic fluid in Indian population. General and comparative endocrinology 241, 100-107.

Singh L., Agarwal T. (2018) PAHs in Indian diet: Assessing the cancer risk. Chemosphere 202, 366-376.

Simon T., Britt J.K., James R.C. (2007). Development of a neurotoxic equivalence scheme of relative potency for assessing the risk of PCB mixtures Regul. Toxicol. Pharmacol., 48 148-170.

Simonich S. L. M., Motorykin O., Jariyasopit N. (2011). PAH intermediates: Links between the atmosphere and biological systems. Chem.-Bio.l Interact. Vol. 192. 26-29.

Singh L., Agarwal T. (2018). PAHs in Indian diet: Assessing the cancer risk. Chemosphere, In press, accepted manuscript, Available online 15 March 2018.

Škrbić B., Marinković V., Spaić S., Milanko V., Branovački S. (2018) Profiles of polycyclic aromatic hydrocarbons in smoke from combustion and thermal decomposition of poplar wood pellets and sawdust. Microchemical Journal 139, 9-17.

Soclo H., Garrigues P., Ewald M. (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Marine pollution bulletin 40(5), 387-396.

Soeder D.J. (2018) The successful development of gas and oil resources from shales in North America. Journal of Petroleum Science and Engineering.

Soto-Jimenez M., Paez-Osuna F. (2001). Cd, Cu, Pb, and Zn in lagoonal sediments from Mazatan harbor (SE Gulf of California): bioavailability and geochemical fractioning. Bull. Environ. Contam. Toxicol. 66, 350 – 356.

Song Q., Zhang Y., Yan L., Wang J., Zhao M. (2017). Risk assessment of the endocrine-disrupting effects of nine chiral pesticides. Journ. of Hazard. Material. Vol. 338. 57-65.

Sole M., Lopez M. J., de Alda M., Porte C., Ladegaard-Pedersen K., Barcelo D. (2000). Estrogenicity determination in sewage treatment plants and surface waters from the Catalonian area (NE Spain) Environ. Sci. Technol., 34. 5076-5083.

Soeder D. J. (2018). The successful development of gas and oil resources from shales in North America. J. Petrol. Sci. Engin. Vol. 163. 399-420.

Spiel D. E., De Leeuw G. (1996). Formation and production of sea spray aerosol. Journal of Aerosol Science 27, S 65 – S 66.

Sporstøl S., Gjøs N., Lichtenthaler R.G., Gustafsen K.O., Urdal K., Oreld F., Skel J. (1983). Source identification of aromatic hydrocarbons in sediments using GC/MS. Environ. Sci. Technol. 17: 282 286

Srivastva N., Vishwakarma P., Bhardwaj Y., Suresh K., Dubey K. (2017). Kinetic and molecular analyses reveal isoprene degradation potential of Methylobacterium sp. Bioresource Technology, Vol 242, 87-91

Strandberg B., Julander A., Sjöström M., Lewné M., Bigert C. (2018). An improved method for determining dermal exposure to polycyclic aromatic hydrocarbons. Chem. Vol. 198. 274-280.

Stuart-Smith S. J., Jepson P. D. (2017). Persistent threats need persistent counteraction: Responding to PCB pollution in marine mammals. Mar. Polic, Vol. 84. 69-75

Stanford B.D., Weinberg H. (2007). Isotope dilution for quantitation of steroid estrogens and nonylphenols by gas chromatography with tandem mass spectrometry in septic, soil, and groundwater matrices. J. Chrom. Vol.1176. 26-36.

Staniszewska M., Graca B., Sokołowski A., Nehring I., Jendzul A. (2017). Factors determining accumulation of bisphenol A and alkylphenols at a low trophic level as exemplified by mussels Mytilus trossulus. Environ. Pollut. Vol. 220.1147-1159.

Staniszewska M., Nehring I., Mudrak-Cegiołka S. (2016). Changes of concentrations and possibility of accumulation of bisphenol A and alkylphenols, depending on biomass and composition, in zooplankton of the Southern Baltic (Gulf of Gdansk). Environ. Pollut. Vol. 213. 489-501.

Stroomberg G. J., Zappey H., Steen R. J. C. A., van Gestel C. A. M., van Straalen N. M. (2004). PAH biotransformation in terrestrial invertebrates—a new phase II metabolite in isopods and springtails. Compar. Biochem. Physiolog. Part C: Toxicol. Pharma. Vol.138. 129-137.

Staniszewska M., Koniecko I., Falkowska L., Krzymyk E. (2015). Occurrence and distribution of bisphenol A and alkylphenols in the water of the gulf of Gdansk (Southern Baltic). Mar. Pollut. Bullet. Vol. 91. 372-379.

Stallones L., Beseler Ch. (2002). Pesticide Poisoning and Depressive Symptoms among Farm Residents. Annal. of Epidem. Vol. 12. 389-394.

Staples C. A., Naylor C. G., Williams J. B., Gledhill W. E., (2001). Ultimate biodegradation of alkylphenol ethoxylate surfactants and their biodegradation intermediates. Environ.Toxicol. Chem 20 (11) : 2450–5.

Strandberg B., Julander A., Sjöström M., Lewné M., Hatice K.A., Bigert C. (2018) An improved method for determining dermal exposure to polycyclic aromatic hydrocarbons. Chemosphere 198, 274-280.

Stroomberg G.J., Zappey H., Steen R.J.C.A., van Gestel C.A.M., Ariese F., Velthorst N.H., van Straalen N.M. (2004) PAH biotransformation in terrestrial invertebrates—a new phase II metabolite in isopods and springtails. Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology 138(2), 129-137.

Staniszewska M., Graca,B., Sokołowski A., Nehring I., Wasik A., Jendzul A. (2017) Factors determining accumulation of bisphenol A and alkylphenols at a low trophic level as exemplified by mussels Mytilus trossulus. Environmental Pollution 220, 1147-1159.

Staniszewska M., Nehring I., Mudrak-Cegiołka S. (2016) Changes of concentrations and possibility of accumulation of bisphenol A and alkylphenols, depending on biomass and composition, in zooplankton of the Southern Baltic (Gulf of Gdansk). Environmental Pollution 213, 489-501.

Sun H., Ge X., Lv Y., Wang A. (2012) Application of accelerated solvent extraction in the analysis of organic contaminants, bioactive and nutritional compounds in food and feed. Journal of Chromatography A 1237, 1-23.

Sun R. X., Lin Q., Ke C. L., Du F. Y., Gu Y. G., Cao K., Luo X. J., Mai B. X. (2016) Polycyclic aromatic hydrocarbons in surface sediments and marine organisms from the Daya Bay, South China. Marine pollution bulletin 103(1-2), 325-332.

Sun Z., Zhu Y., Zhuo S., Liu W., Zeng E.Y., Wang X., Xing B., Tao S. (2017) Occurrence of nitro- and oxy-PAHs in agricultural soils in eastern China and excess lifetime cancer risks from human exposure through soil ingestion. Environment International 108, 261-270.

Sun Z. Y., Zhu S., Zhuo W., Tao S. (2017). Occurrence of nitro- and oxy-PAHs in agricultural soils in eastern China and excess lifetime cancer risks from human exposure through soil ingestion. Environ. Intern. Vol.108. 261-270.

Sun H., X Ge., Lv Y., Wang A. (2012). Application of accelerated solvent extraction in the analysis of organic contaminants, bioactive and nutritional compounds in food and feed. J. Chromatograph. Vol. 1237. 1-23.

Suciu N. A., Lamastra L., Trevisan M. (2015). PAHs content of sewage sludge in Europe and its use as soil fertilizer. Waste Manag. Vol. 41. 119-127.

Syakti A.D., Hidayati N.V., Hilmi E., Piram A., Doumenq P. (2013) Source apportionment of sedimentary hydrocarbons in the Segara Anakan Nature Reserve, Indonesia. Marine pollution bulletin 74(1), 141-148.

Takazawa Y., Takasuga T., Doi K., Saito M., Shibata Y. (2016). Recent decline of DDTs among several organochlorine pesticides in background air in East Asia. Environ. Poll. Vol. 217. 134-142.

Tan B., Mohd M.A. (2003). Analysis of selected pesticides and alkylphenols in human cord blood by gas chromatograph-mass spectrometer. Talanta 61. 385 – 391.

Tarafdar A., Sinha A. (2018). Public health risk assessment with bioaccessibility considerations for soil PAHs at oil refinery vicinity areas in India. Sci. Tot. Environ. Vol. 616–617. 1477-1484.

Tehrani G. M., Hashim R., Sulaiman A. H., Sany S. B. T., Salleh A., Jazani R. Kh., Savari A., Barandoust R. F. (2013). Distribution of total petroleum hydrocarbons and polycyclic aromatic hydrocarbons in Musa bay sediments (northwest of the Persian Gulf). Jour. Envir. Protect. Eng. Vol. 39. 115—128.

Thomas J. R., Bowler R. M., Rauch S. S., Pedroza G. I. (1992). Pesticide exposure and neuropsychological impairment in migrant farm workers. Arch. of Clinic. Neuropsyc. Vol. 85-95.

Thoumelin G. 1995. Surfactants in fresh and marine waters. Reperes Ocean Rapport. 1995.

Tian H., Li Y., Wang W., Wu P., Ru S. (2012). Exposure to monocrotophos pesticide during sexual development causes the feminization/demasculinization of the reproductive traits and a reduction in the reproductive success of male guppies (Poecilia reticulata). Toxicol. and Appli. Pharmacol. Vol. 263. 163-170.

Tongo I., Ogbeide O., Ezemonye L. (2017). Human health risk assessment of polycyclic aromatic hydrocarbons (PAHs) in smoked fish species from markets in Southern Nigeria. Toxicol. Rep. Vol. 4. 55-61.

Tolosa I., Bayona J. M., Albaiges J. (1995) Spatial and temporal distribution, fluxes and budgets of organochlorinated compounds in northwest Mediterranean sediment. Environ Sci. Technol. 29: 2519 2527

Tolosa I., Stephen J., de Mora S., Fowler W., Villeneuve J., Cattini C. (2005). Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf and the Gulf of Oman. Mar. Pollut. Bullet. Vol.50. 1619-1633.

Torres P., da Cunha R. T., Micaelo C., dos A., Rodrigues S. (2016). Bioaccumulation of metals and PCBs in Raja clavata. Sci.Tot. Environ.Vol. 573.1021-1030.

Tranchida G., Bellanca A., Angelone M., Bonanno A., Patti B. (2010). Chronological records of metal deposition in sediments from the Strait of Sicily, central Mediterranean: Assessing natural fluxes and anthropogenic alteration. J. Mar. Sys. Vol.79. 157-172.

Tudoran M., Putz M. (2012) Polycyclic Aromatic Hydrocarbons: from In Cerebro to In Silico Eco-Toxicity Fate. Chem Bull Politehnica Univ (Timisoara) 57(71), 50-53.

Uguz C., Iscan A., Erguven B., Togan I. (2003). The bioaccumulation of nonylphenol and its adverse effect on the liver of rainbow trout (Oncorhynchus mykiss). Environ. Res. 92. 262-270.

Umar Z. D., Abd.Aziz N. A., Zahmir S., Muskhazli Z. (2017). Rapid biodegradation of polycyclic aromatic hydrocarbons (PAHs) using effective Cronobacter sakazakii MM045 (KT933253). MethodsX. Vol. 4.104-117.

Uno S., Kokushi E., Añasco N. C., Iwai T., Koyama J. (2017). Oil spill off the coast of Guimaras Island, Philippines: Distributions and changes of polycyclic aromatic hydrocarbons in shellfish. Mar. Poll. Bulletin. Vol. 124. 962-973.

United Nations Environment Program, UNEP/IOC/IAEA (1992) Determination of petroleum hydrocarbons in sediments. Reference Methods for Marine Pollution Studies 20, UNEP, 75p.

United Nations Environment Program, UNEP (2001) Stockholm CONVENTION on POPs, Text and Annexes, Interim Secretariat for the Stockholm Convention on Persistent Organic Pollutants. UNEP Chemicals, Switzerland

United Nations Environment Program, UNEP (2002) Regionally Based Assessment of Persistent Toxic Substances. Mediterranean regional report. Global Environment Facility, 161p.

United Nations Environment Program, UNEP (2003) Stockholm Convention: Master List of Action: on the reduction and /or elimination of the releases of persistent organic pollutants. Gevena, Swizerland.

US EPA. (2010). Nonylphenol (NP) and nonylphenol ethoxylates (NPEs) action plan.

US EPA. (2000). Deposition of AirPollutants to the GreatWaters : Third Report to Congress. Office of Air Quality Planning and Standards. EPA-453/R-00-0005; June 2000. http://www.epa.gov/air/oaqps/gr8water/3rdrpt/index.html

US EPA (Environmental Protection Agency). Polycyclic aromatic hydrocarbons (PAHs) — EPA fact sheet. Washington (DC): National Center for Environmental Assessment, Office of Research and Development; (2008).

Vaezzadeh V., Pauzi Zakaria M., Tan Shau-Hwai A., Zaiton Ibrahim Z., Mustafa S., Keshavarzifard M., Mohsen Magam S., Abdullah Abdo Alkhadher S. (2015) Source type evaluation of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the Muar River and Pulau Merambong, Peninsular Malaysia. Environmental Forensics 16(2), 135-142.

Valcke M., Bourgault M., Rochette L., Normandin L., Phaneuf D. (2017). Human health risk assessment on the consumption of fruits and vegetables containing residual pesticides: A cancer and non-cancer risk/benefit perspective. Environ. Intern. Vol. 108. 63-74.

Van Ry D. A., Dachs J., Gigliotti C. L, Brunciak P. A., Nelson E. D., Eisenreich S. J. (2000). Atmospheric Seasonal Trends and Environmental Fate of Alkylphenols in the Lower Hudson River Estuary. Environ. Sci. Technol. 34. 2410–2417.

Venturini N., Bícego M. C., Taniguchi S., Sasaki S. T, García-Rodríguez F., Brugnoli E., Muniz P. (2015). A multi-molecular marker assessment of organic pollution in shore sediments from the Río de la Plata Estuary, SW Atlantic. Mar. Poll. Bull.461–475.

Venkatesan A. K., Halden R. U. (2014). Wastewater Treatment Plants as Chemical Observatories to Forecast Ecological and Human Health Risks of Manmade Chemicals. Sci. Rep. vol. 4. Articl. Num. 3731.

Vethaak A. D., Lahr J., Schrap S. M., Belfroid A. C., Rijs G. B. J., Gerritsen A., de Boer J., Bulder A S., Grinwis G. C. M., Kuiper R. V., Legler J., Murk T. A. J., Peijnenburg W., Verhaar H. J. M., de Voogt. P. (2005). An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands. Chemosphere 59, 511 – 524.

Vikelsoe J., Thomsen M., Johansen E., Carlsen L. (1999) Phthalates and nonylphenols in soil. A field study of different soil profiles. National Environmental Research Institute, Rocksilde.

Vilela S. L., Bassin J. P., Peixoto R. S. (2018). Water contamination by endocrine disruptors: Impacts, microbiological aspects and trends for environmental protection. Environ. Poll. Vol. 235. 546-559.

Wang H., Qu B., Liu H., Ding J., Ren N. (2018). Analysis of organochlorine pesticides in surface water of the Songhua River using magnetoliposomes as adsorbents coupled with GC-MS/MS detection. Sci. of The Tot. Environ. Vol. 618. 70-79.

Wang Y., Zhang S., Cui W., Meng X., Tang X. (2018). Polycyclic aromatic hydrocarbons and organochlorine pesticides in surface water from the Yongding River basin, China: Seasonal distribution, source apportionment, and potential risk assessment. Sci. of The Tot. Environ. Vol. 618. 419-429.

Wang Z., Ren P., Sun Y., Ma X., Liu X., Na G., Yao Z. (2013). Gas/particle partitioning of polycyclic aromatic hydrocarbons in coastal atmosphere of the north Yellow Sea. China. Environ. Sci. Pollut. Res. Int. 20, 5753e5763.

Wang D., Wang Y., Singh V.P., Zhu J., Jiang L., Zeng D., Liu D., Zeng X., Wu J., Wang L. (2018) Ecological and health risk assessment of PAHs, OCPs, and PCBs in Taihu Lake basin. Ecological Indicators 92, 171-180.

Wang H. S., Cheng Z., Liang P., Shao D. D., Kang Y., Wu S. C., Wong C.K., Wong M.H. (2010) Characterization of PAHs in surface sediments of aquaculture farms around the Pearl River Delta. Ecotoxicology and Environmental Safety 73(5), 900-906.

Wang J. Z., Zhang K., Liang B. (2012) Tracing urban sewage pollution in Chaohu Lake (China) using linear alkylbenzenes (LABs) as a molecular marker. Science of The Total Environment 414, 356-363.

Wang J., Liu J., Ling W., Huang Q., Gao Y. (2017) Composite of PAH-degrading endophytic bacteria reduces contamination and health risks caused by PAHs in vegetables. Science of The Total Environment 598, 471-478.

Wang Y., Lai D., Latino K., Fenner D., Helbling. (2018). Evaluating the environmental parameters that determine aerobic biodegradation half-lives of pesticides in soil with a multivariable approach. Chem. Vol. 209. 430-438.

Wang R. Z., Xu T L., Yu L. Z., Zhu J J., Li X. Y. (2013). Effects of land use types on surface water quality across an anthropogenic disturbance gradient in the upper reach of the Hun River, Northeast China. Environ. Monit. Assess. 185. 4141 – 51.

Wania F., Mackay D. (1996). Tracking the distribution of persistent organic pollutants. Environ. Sci. Technol. 30 (9), 390A–396A..

Warhurst A M. (1995). An environmental assessment of alkylphenol ethoxylates and alkylphenols. Friends of the Earth. London, UK, 1-15.

Wahlang B., Prough R.A., Falkner K.C., Hardesty J.E., Song M., Clair H.B., Clark B.J., States, J.C., Arteel M.C. (2016). Cave Polychlorinated biphenyl-xenobiotic nuclear receptor interactions regulate energy metabolism, behavior, and inflammation in non-alcoholic-steatohepatitis Toxicol. Sci., 149. 396-410

Wahlang B., Perkins J T., Michael Petriello C., Hoffman J. B.., Hennig B. (2017). A compromised liver alters polychlorinated biphenyl-mediated toxicity. Toxicol. Vol. 380, 11-22.

Weber G., Christmann N., Thiery A., Martens D., Kubiniok J. (2018). Pesticides in agricultural headwater streams in southwestern Germany and effects on macroinvertebrate populations. Sci. of The Tot. Environ, Vol. 619–620. 638-648.

Westlund P., Yargeau V. (2017). Investigation of the presence and endocrine activities of pesticides found in wastewater effluent using yeast-based bioassays. Sci. of The Tot. Environ, Vol. 607–608. 744-751.

Wei G. L., Liu L. Y., Bao L.J., Zeng E.Y. (2014) Tracking anthropogenic influences on the continental shelf of China with sedimentary linear alkylbenzenes (LABs). Marine pollution bulletin 80(1-2), 80-87.

Wershaw R. (1993). Model for Humus in Soils and Sediments. Environ. Sci. Technol., 1993, 27 (5), pp 814–816

Wee S. Y., Aris A Z (2017). Ecological risk estimation of organophosphorus pesticides in riverine ecosystems. Chem.Vol. 188. 575-581.

WHO (World Health Organization) (2003). Polynuclear aromatic hydrocarbons in drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality ; 2003 (WHO/SDE/WSH/03.04/59).

White R., Jobling S., Hoare S. A., Sumpter J. P., Parker M. G. (1994). Environmentally ersistent alkylphenolic compounds are estrogenic. Endocrinology 135 (1)175–182.

Wilson N. K., Chuang J. C., Luyu C. (2001). Levels of persistent organic pollutants in several child day care centers. J. Expo. Anal. Environ. Epidemiol. 11:449 – 458.

Witt G., Trost E. (1999). Polycyclic aromatic hydrocarbons (PAHs) in sediments of the Baltic Sea and of the German coastal waters. Chemosphere 38(7), 1603-1614

Wild S. R., Jones K. C. (1995). Polynuclear aromatic hydrocarbons in the United Kingdomenvironment: a preliminary source inventory and budget. Environ. Pollut. 88. 91–108.

Wild S. R., Waterhouse K. S., McGrath S. P., Jones K. C. (1990). Organic contaminants in an agricultural soil with a known history of sewage sludge amendments: polycyclic aromatic hydrocarbons. Environ. Sci. Tech. 24.1706 – 11.

Wu L., Chang H., Ma X. (2017). A modified method for pesticide transport and fate in subsurface environment of a winter wheat field of Yangling, China. Sci. of The Tot. Environ. Vol. 609. 385-395.

Xiao P., Mori T., Kamei I., Kiyota H., Kondo R. (2011). Novel metabolic pathways of organochlorine pesticides dieldrin and aldrin by the white rot fungi of the genus Phlebia. Chem.Vol. 85. 218-224.

Xu E. G. B., Morton B., Lee J. H. W., Leung K. M. Y. (2015). Environmental fate and ecological risks of nonylphenols and bisphenol A in the Cape D'Aguilar Marine Reserve, Hong Kong. Marine Pollution Bulletin, Volume 91, Issue 1, 15 February 2015, Pages 128-138.

Xue R., Chen L., Lu Z., Wang J., Yang H., Zhang J., Cai M. (2016) Spatial distribution and source apportionment of PAHs in marine surface sediments of Prydz Bay, East Antarctica. Environmental Pollution 219, 528-536.

Xie Z., Lakaschus S., Ebinghaus R., Caba A., Ruck W. (2006). Atmospheric concentrations and air-sea exchanges of nonylphenol, tertiary octylphenol and nonylphenol monoethoxylate in the North Sea. Environ Poll 142: 170-180.

Yang G. P. (2000) Polycyclic aromatic hydrocarbons in the sediments of the South China Sea. Environmental Pollution 108(2), 163-171.

Yang W., Lang Y. H., Bai J., Li Z. Y. (2015) Quantitative evaluation of carcinogenic and non-carcinogenic potential for PAHs in coastal wetland soils of China. Ecological Engineering 74, 117-124.

Yang X., Liu S., Xu Y., Liu Y., Chen L., Tang N., Hayakawa K. (2017) Emission factors of polycyclic and nitro-polycyclic aromatic hydrocarbons from residential combustion of coal and crop residue pellets. Environmental Pollution 231, 1265-1273.

Yoo J. C., Lee C. D., Yang J. S., Baek K. (2013) Extraction characteristics of heavy metals from marine sediments. Chemical engineering journal 228, 688-699.

Yan C., Zheng M., Yang Q., Zhang Q., Zhu Y. (2015). Commuter exposure to particulate matter and particle-bound PAHs in three transportation modes in Beijing, China. Environ. Pollut. Vol. 204. 199-206.

Yang Ch., Shuang C., Yu Y., Yue X., Yu L., Shu L., Wen T., Liu X. (2018). Emission characteristics of polycyclic aromatic hydrocarbons from pyrolytic processing during dismantling of electronic wastes. J. Hazard. Material. Vol. 351. 270-276.

Yoo J., Lee C., Yang C., Baek K. (2013). Extraction characteristics of heavy metals from marine sediments. Chem. Engin. J. Vol. 228. 688-699.

Yang W., Lang Y., Bai J., Li Z. (2015). Quantitative evaluation of carcinogenic and non-carcinogenic potential for PAHs in coastal wetland soils of China. Ecol. Engin. Vol. 74. 117-124.

Yang X., Liu S., Xu Y., Liu Y., Hayakawa K. (2017). Emission factors of polycyclic and nitro-polycyclic aromatic hydrocarbons from residential combustion of coal and crop residue pellets. Environ. Poll. Vol. 231.1265-1273.

Ying G. G., Williams B., Kookana R. (2002). Environmental fate of alkylphenols and alkylphenol ethoxylates--a review Environ Int. 28. 215 - 26.

Ying G. G. (2006). Fate, behavior and effects of surfactants and their degradation products in the environment. Environ. Inter.Vol.32. p. 417-431.

Zaffar H., Irshad U., Pervez A., Naqiv T. A. (2016). Mode of Action, Toxicity and Biodegradation of Organchlorinated Pesticides: A Mini Overview. J. Appl. Environ. Biol. Sci. 6(8)1-6, 2016.

Zengel S., Weaver J., Wilder S. L., Dauzat J., Nixon Z. (2018). Vegetation recovery in an oil-impacted and burned Phragmites australis tidal freshwater marsh. Sci. Tot. Environ. Vol. 612. 231-237.

Zhang Y., Lin Y., Cai J., Liu Y., Zheng M. (2011). Atmospheric PAHs in North China: Spatial distribution and sources. Sci. Tot. Environ. Vol. 565. 994-1000.

Zhang K., Wang J., Liang B., Shen R., Zeng E. Y. (2012). Assessment of aquatic wastewater pollution in a highly industrialized zone with sediment linear alkylbenzene. Environmental Toxicology and Chemistry, Vol. 31. 724–730.

Zhao O. Y., Zhang X.N., Feng S.D., Zhang L.X., Shi W., Yang Z., Chena M.M., Fanga X.D. (2017). Starch-enhanced degradation of HMW PAHs by Fusarium sp. in an aged polluted soil from a coal mining area. Chemosphere 174, 774 – 780.

Zhou S., Tong L., Tang Q., Gu X., Liu W. (2013). Residues, sources and tissue distributions of organochlorine pesticides in dog sharks (Mustelus griseus) from Zhoushan Fishing Ground, China. Mar. Poll. Bull. Vol. 73. 374-380.

Zhang H., Spiteller M., Guenther K., Boehmler G., Zuehlke S. (2009). Degradation of a chiral nonylphenol isomer in two agricultural soils. Environ. Pollut. 157.1904 – 1910.

Zhang J., Fan S., Zhang M., Grieneisen M. L., Zhang J. (2018). Aliphatic hydrocarbons recovered in vegetables from soils based on their in-situ distribution in various soil humus fractions using a successive extraction method. J. Hazard. Mat. Vol. 346.10-18.

Zeng Q., Jeppesen., Gu V., Mao Z., Chen H. (2018). Distribution, fate and risk assessment of PAHs in water and sediments from an aquaculture- and shipping-impacted subtropical lake, China. Chem. Vol. 201. 612-620.

Zhang X., Gao Y., Qingzhao L.Q., Li G., Guo Q., Yan C. (2011). Estrogenic compounds and estrogenicity in surface water, sediments, and organisms from Yundang Lagoon in Xiamen, China. Archives of Environmental Contamination and Toxicology. 2011;61:93–100. doi: 10.1007/s00244-010-9588-0.

Zhang A., Zhao S., Wang L., Yang X., Zhao Q., Fan J., Yuan X. (2016) Polycyclic aromatic hydrocarbons (PAHs) in seawater and sediments from the northern Liaodong Bay, China. Marine pollution bulletin 113(1-2), 592-599.

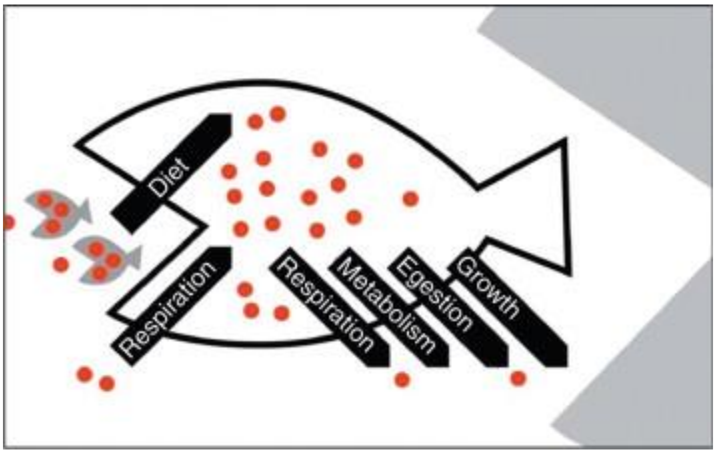
Zhang H., Du M., Jiang H., Zhang D., Lin L., Ye H., Zhang X. (2015) Occurrence, seasonal variation and removal efficiency of antibiotics and their metabolites in wastewater treatment plants, Jiulongjiang River Basin, South China. Environmental Science: Processes & Impacts 17(1), 225-234.

Zhang J., Fan S., Zhang M., Grieneisen M.L., Zhang J. (2018) Aliphatic hydrocarbons recovered in vegetables from soils based on their in-situ distribution in various soil humus fractions using a successive extraction method. Journal of Hazardous Materials 346, 10-18.

Zoller U., Sosis P. (2009). Handbook of detergents. CRC Press, cop. 2009. Surfactant science series, Vol. 142

Zhu Z., Zhuo Z., Yuegang Z. (2011). Bisphenol A and other alkylphenols in the environment - occurrence, fate, health effects and analytical techniques. Advances in environmental research. Vol. 2 pp.179-202.

List of Definitions

Terms	Definitions
Allochthonous	Denoting a deposit or formation that originated at a distance from its present position. Often contrasted with autochthonous Allochthonous also refers to material that has been imported into an ecosystem. While an ecosystem involves both organic (plants, bacteria, animals) and inorganic things (rocks, soil, water), the allochthonous material that enters an ecosystem refers to organic matter and its nutrients, such as nitrogen and phosphorous. Allochthonous material commonly resides in an aquatic ecosystem, such as a stream or river.
Biococentration factor (BCF)	Bioconcentration factor (BCF) can be expressed as the ratio of the concentration of a chemical in an organism to the concentration of the chemical in the surrounding environment. BCF is expressed in units of liter per kilogram (ratio of mg of chemical per kg of organism to mg of chemical per liter of water).
Bioaccumulation	Bioaccumulation of contaminants (dots) to an organism (fish) is a net result of uptake and loss processes (arrows). Uptake is direct from the water by respiration and indirect through the diet. Examples of loss processes are respiration, metabolism, egestion, and growth dilution. Bioaccumulating chemicals increase more than 5000 times from the water to the animal. As the total biomass decreases per trophic level in the food chain (while the contaminants remain), the contaminant concentrations increase moving up the food chain.  Figure 1. Bioaccumulation processes
Emerging pollutants	Compounds that are not currently covered by existing water - quality regulation – have not been studied before and are thought to be potential threat to the environmental ecosystem and human health and safety. Not necessarily new compounds Some are present in the environment for decades Recently “discovered” – improvement of analytical techniques

	Environmental and health significance under evolution
EC$_{50}$	In ecotoxicity, EC$_{50}$ (median effective concentration) is the concentration of test substance which results in a 50 percent reduction in either algae growth (EbC$_{50}$) or algae growth rate (ErC$_{50}$) or Daphina immobilization. They are often obtained from acute aquatic oxicity studies. The units of EC$_{50}$ are mg/L. EC$_{50}$ values are often used for acute enviromental hazard classification and calculation of predicted non-effect concentration (PNEC).
LC$_{50}$/LD$_{50}$	LD$_{50}$ (Lethal Dose 50%) is a statistically derived dose at which 50% of the animals will be expected to die. For inhalation toxicity, air concentrations are used for exposure values. Thus, the LC$_{50}$ (Lethal Concentration 50%) is used.
NOEL	No-observed-effect level (NOEL): greatest concentration or amount of a substance, found by experiment or observation, that causes no alteration of morphology, functional capacity, growth, development, or lifespan of the target organism distinguishable from those observed in normal (control) organisms of the same species and strain under the same defined conditions of exposure.
LOEL	The Lowest Observed Effect Level is the lowest tested dose or exposure level at which, in a study, a statistically significant effect is observed in the exposed population compared with an appropriate control group.
Turbulence	In fluid dynamics, turbulence or turbulent flow is any pattern of fluid motion characterized by chaotic changes in pressure and flow velocity. It is in contrast to a laminar flow regime, which occurs when a fluid flows in parallel layers, with no disruption between those layers. Turbulence is commonly observed in everyday phenomena such as surf, fast flowing rivers, bllowing storm clouds, or smoke from a chimney, and most fluid flows occurring in nature and created in engineering applications are turbulent. Turbulence is caused by excessive kinetic energy in parts of a fluid flow, which overcomes the damping effect of the fluid's viscosity.

Upwelling

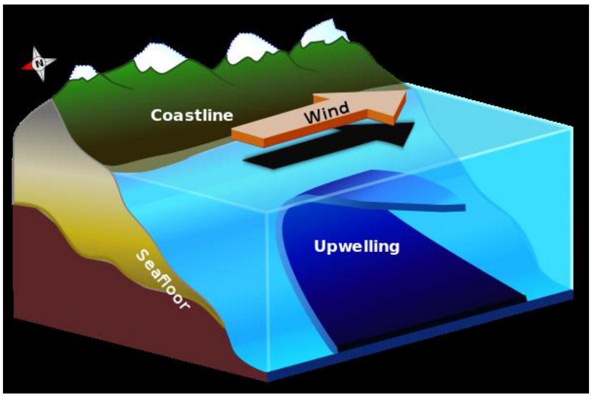


Figure 2. Upwelling processes as the influence of the wind energy and the bathymetric condition.

an oceanographic phenomenon that involves wind-driven motion of dense, cooler, and usually nutrient-rich water towards the ocean surface, replacing the warmer, usually nutrient-depleted surface water. The nutrient-rich upwelled water stimulates the growth and reproduction of primary producers such as phytoplankton. Due to the biomass of phytoplankton and presence of cool water in these regions, upwelling zones can be identified by cool sea surface temperatures (SST) and high concentrations of chlorophyll-a.

The increased availability of nutrients in upwelling regions results in high levels of primary production and thus fishery production. Approximately 25% of the total global marine fish catches come from five upwellings that occupy only 5% of the total ocean area. Upwellings that are driven by coastal currents or diverging open ocean have the greatest impact on nutrient-enriched waters and global fishery yields.

Persistent organic pollutants (POPs)

Persistent organic pollutants (POPs) are chemicals of global concern due to their potential for long-range transport, persistence in the environment, ability to bio-magnify and bio-accumulate in ecosystems, as well as their significant negative effects on human health and the environment. Humans are exposed to these chemicals in a variety of ways: mainly through the food we eat, but also through the air we breathe, in the outdoors, indoors and at the workplace. Many products used in our daily lives may contain POPs, which have been added to improve product characteristics, such as flame retardants or surfactants. As a result, POPs can be found virtually everywhere on our planet in measurable concentrations.

Non-ionic surfactant

Non-ionic surfactant refers to a kind of surfactant with its molecule not undergoing ionization when being dissolved in water. According to their different hydrophilic groups, it can be divided into polyoxyethylene and polyols two categories.

1. Polyoxyethylene: its formula is RO $(CH_2CH_2O)_nH$. It is manufactured through the reaction between the active hydrogen-containing compound and the ethylene oxide. Commonly used active hydrogen-containing compound in industry include fatty alcohols, alkylphenols, fatty acids, fatty amines, fatty amides, polyhydric alcohols, fatty acid esters, oil lipid, sorbitol and so on. The largest category of commercially available nonionic surfactants is the ethylene oxide adducts of the fatty alcohol and alkylphenol. Polyoxyethylene type surfactant is mostly soluble in water with very wide range of applications and used as cleaning agents, penetrating agents, leveling agents and emulsifiers in many industrial sectors.

2. Polyhydric alcohol type: it is the amide type or esters type compound manufactured from the reaction between multi-hydroxyl containing compounds with fatty acid. Polyol-type nonionic surfactant has high safety, small irritant effect on the skin, so in addition to be used as the oil agent and softener of the fiber, it can also be used as emulsifiers and dispersing agents in the food industry, the pharmaceutical industry and the cosmetics industry.

Anionic surfactants

The anionic surfactant can undergo dissociation when being dissolved in water with the part of surface activity exhibiting hydrophobic anion effects. Typical anionic surfactants include soaps, alkylbenzene sulfonates, alkyl sulfonates, alkyl sulfates, salts of fluorinated fatty acids, silicones, fatty alcohol sulfates, polyoxyethylene fatty alcohol ether sulfates, α-olefin sulfonate, polyoxyethylene fatty alcohol phosphates ether, alkyl alcohol amide, alkyl sulfonic acid acetamide, alkyl succinate sulfonate salts, amino alcohol alkylbenzene sulfonates, naphthenates, alkylphenol sulfonate and polyoxyethylene monolaurate.

Anionic surfactants are generally insoluble at low temperatures. If the concentration continued to increase, they will reach a threshold limit, then precipitating out active agent of hydration. Upon increased water temperature at a certain temperature, due to the dissolving of the micelles, leaving the solubility being rapid increased with this temperature point called as catastrophe point. This feature is hold by ionic surfactants.

Wastewater treatment plants (WWTP)

a process used to convert wastewater into an effluent that can be returned to the water cycle with minimum impact on the environment, or directly reused. The latter is called water reclamation because treated wastewater can then be used for other purposes. The treatment process takes place in a wastewater treatment plant (WWTP), often referred to as a Water Resource Recovery Facility (WRRF) or a sewage treatment plant. Pollutants in municipal wastewater (households and small industries) are removed or broken down.

The treatment of wastewater is part of the overarching field of sanitation. Sanitation also includes the management of human waste and solid waste as well as stormwater (drainage) management. By-products from wastewater treatment plants, such as screenings, grit and sewage sludge may also be treated in a wastewater treatment plant.

Figure 3. How WWTPs connecting to the industrial and domestic activities.