An insight into ecotoxicological significance of PAHs contamination in selected Kenyan estuaries

Wanjeri V.O¹ , Okuku E.O1, *, Ohowa B.O¹ , Kosore M.C.¹ , Ongore C.O1,

¹Kenya Marine and Fisheries research Institute, P.O. Box 81651, Mombasa, Kenya.

²Catholic University Leuven, Department of Earth and Environmental Sciences, Kasteelpark Arenberg 20, B-3001 Heverlee, Belgium.

³School of Environmental Studies, Moi University, P.O. Box 3900, Eldoret, Kenya.

*Corresponding author E-mail: ochiengokuku2003@yahoo.com. Tel: +254726215339. Fax: +254 (020) 2353226

Accepted 30 May 2013

Sediments samples from 8 selected locations along Kenyan major estuaries were analysed for PAH concentrations by gas chromatography-mass spectrophotometer. The total PAH concentrations in the sampled sites were found to be relatively low with a mean of 4.44 ng g¹ . Tana estuary had the highest levels of total PAHs (mean 7.22 ng g-1), while the reference location (Ramisi) had the lowest concentration (mean 0.33 ng g-1). Sediments grain size, organic matter and total organic carbon had no significant effect on PAH concentrations. All the stations were dominated by LMW PAHs apart from Tana 3 and 4 that also had substantial amount of HMW PAHs. The Fl/Fl+Pyr ratio showed that PAHs in 7 of the studied locations were primarily derived from petroleum sources except Sabaki bridge station that also had petroleum combustion sources. The levels of both individual and total PAHs in all the sampling sites were found to be significantly lower than the Effects Range Low and as such no significant ecological threats are expected.

Keywords: Organics contamination, estuarine, ecotoxicology, polycyclic aromatic hydrocarbons, sediments.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) with two or more fused rings form a wide group of ubiquitous environmental persistent organic pollutants (POPs). The composition of PAH mixtures in soils worldwide is dominated by two major source patterns. One source pattern is the background signal dominated by natural PAHs produced biologically, e.g., by endophytic fungus (Daisy et al., 2002), synthesis by termites or associated microorganisms (Wilcke et al. 2000), and in anaerobic soils and sediments (Venkatesan 1988). The background signal also includes ubiquitous atmospherically distributed anthropogenic emissions (Wilcke 2007).

The other source pattern arises from the combustion of fossil fuels dominated by high-molecular weight PAHs (HMW PAHs) irrespective of the different fuels and combustion conditions (Wilcke 2007). They include those formed from partial combustion of fuels (coal, oil, gas, wood), garbage, motor vehicles, waste incineration, home heating, oil refining, coke and asphalt production, or other organic substances like tobacco or charbroiled meat (Nadal et al 2004; Patrolecco et al., 2010). The other common source of PAHs is the accidental spillage of fossil fuels, including crude oils and refined oil products

such as petrol (Qiao et al., 2006). They are also introduced into the environment via natural combustion processes such as volcanic eruption, forest and prairie fires (Kim et al. 2003).

PAHs are resistant to environmental degradation, leading to their ubiquitous distribution (Kim et al., 2003). They have low aqueous solubility, high lipophilicity (hydrophobicity) and tend to associate with particulate and dissolved organic matter in the aquatic environment. Sediments act as the ultimate sink for air and waterborne PAHs thus reflecting the inputs for an ecosystem (Patrolecco, 2010; Qiao et al., 2006). In rivers, sediment can act as a transient storage compartment for PAHs under specific hydrodynamic conditions but in the event of bioturbation, PAHs can be re-suspended or redissolved thus becoming bioavailable (Katayama et al., 2010; Patrolecco et al., 2010).

Organisms living in PAH-contaminated environments can absorb these compounds through their body surface and gills or by ingestion of contaminated sediment or particles, bioaccumulate and then transfer the contaminants through the aquatic food web. Several PAHs have been shown to have a number of potential

adverse effects on humans and wildlife, such as carcinogenicity, mutagenicity and teratogenicity (Guo et al., 2010; Kim et al., 2003; Tang et al., 2005; Qiao et al., 2006; Qin et al., 2011).

In general, PAHs have been detected around the world at sites which are located even far away from industrial activity such as the Polar Regions, and in the tropics. This wide distribution could result into fractionation of the PAHs according to the volatility of the individual compounds. Besides the global fractionation by longrange transport, PAH fractionation can also occur at the local scale along short-distance from point emitters of PAHs (Meharg et al., 1998; Wilcke et al., 1996, 2007). Thus, atmospheric transport of PAHs changes the PAH composition and might be one control of systematic differences in soil/sediments PAH patterns across different climatic zones.

PAHs are one of the environmental contaminants of greatest concern on regional and global scales due to their long-range transport properties, environmental persistence, and potential health risks,(Guo et al., 2010 ; Wilcke et al., 2007). However, no information is available regarding sedimentary PAHs contamination in Western Indian Ocean (WIO) region, and specifically along the Kenyan coastline. Furthermore, the available PAH data are from localised studies that cannot be relied on to provide the general distribution of PAH along the Kenya Coast. Moreover, such studies did not attempt risk assessment thus the results are not of direct importance in informing management interventions. The purpose of this study was therefore to 1) establish the background levels of PAHs in sediments from selected Kenyan estuarine systems to serve as essential reference information for future studies, 2) determine the source(s) and composition of sediment PAHs in these estuaries in order to inform formulation of adequate PAHs control strategies and 3) to screen for potential ecological threat that could arise from sediments' PAHs contamination.

MATERIALS AND METHODS

Study area

The sites sampled were located in rivers the Tana, Sabaki and Ramisi estuaries (Figure 1). The Sabaki River originates from Ngong hills in central Kenya (as River Athi). It flows mainly through sand and rocks and mining industries for cement and other inorganic products as Athi River. It further flows through areas with major industries and coffee and tea farms where agrochemicals and fertilizers are used in large scale before discharging into the Indian Ocean. Ramisi river estuary is located at Funzi Bay. The Ramisi River flows through Shimba Hills and later through an area extensively covered by different mangrove species before discharging into the Indian Ocean. The Tana River is the largest river in Kenya,

arising on the south-western flank of Mount Kenya. With a drainage basin of 120,000 km² (Ongwenyi et al., 1993a), Tana River flows for 1012 km and discharges into the Indian Ocean near Tana (Saha 1982).

Sample collection and storage

About 100 to 200g of top 1 cm surface sediment samples were collected from selected locations in the Tana, Sabaki and Ramisi estuarine systems (Figure 1). The samples were put in aluminium containers previously cleaned with hexane HPLC grade (Scharlau Chemie, S.A., Spain) and stored in a cool box at low temperature $(4^{\circ}C)$ to limit biological and chemical activities. The samples were then transported to Kenya Marine and Fisheries Research Institute laboratory and kept frozen at -20^oC before transportation to the Laboratory of Physics and Toxico-Chemistry (LPTC) at the University of Bordeaux 1, France for analysis.

Sample preparation and extraction

In the laboratory, about 100g of sediment samples were wet weighed, put in clean pre-weighed aluminium containers and covered with clean aluminium sheets with holes then freeze dried for 48 hours using Heto power dry LL 3000 freeze-dryer (Thermo Scientific). After freezedrying, the samples were weighed to obtain the dry weight, sieved through a 2 mm mesh sized metallic sieve to remove any coarse materials. The samples were then stored in clean well labelled glass Amber bottles to protect them from light awaiting analysis.

During the extraction process, about 3g of sample were put in the digestion containers and 30 µl of internal standard containing a mixture of per-deuterated PAHs; Phenanthrene-d₁₀, benzo[a]pyrene- d_{12} , benzo[e]pyrene d_{12} and benzo[g,h,i]perylene- d_{12} (Cambridge Isotope Laboratories, Andover, USA); and Fluoranthene- d_{10} , chrysene-d₁₂ and pyrene-d₁₀ (MSD isotopes, Division of Merck Frost Canada INC, Montreal, CND) was added. The added internal standard was used to quantify recovery of the total extraction procedure. The samples were extracted for 20 minutes with 30 ml dichloromethane (Pro-labo, Fontenay-sous-Bois, France) using START E microwave assisted extraction system (Milestone, Italy). The extracts were mechanically filtered into 25 ml Amber glass vials through clean glass funnels stuffed with pre-cleaned glass wool.

The filtered extracts were concentrated to about 1 ml using Rapidvap LABCONCO (Serlabo Technologies, France). The concentrated samples were then subjected to clean-up process during which the lipids and sulfur were removed from the extracts using a micro-column containing alumina-activated copper. The extracts were then purified on the micro-column containing alumina by

Figure 1. Kenya coastline showing the selected sampling locations in the Tana, Sabaki and Ramisiestuarine systems.

elution with 15 ml dichloromethane and fractionated on micro-column containing silica in order to separately collect saturated and aromatic compounds (analytes). Copper (40 mesh, 99.5% purity, Aldrich, Saint Quentin Fallavier, France) was activated with hydrochloric acid (7M), then washed with water, acetone, and dichloromethane. Alumina (150 basic, type T, 0.063 ± 0.2 mm) and silica (Silica gel, 0.063 ± 0.2 mm, Merck,

Darmstadt, Germany) were washed with dichloromethane, activated and stored at 150^ºC to prevent uptake of water. The samples extracts were eluted respectively with 6 ml pentane and a mixture of pentane/dichloromethane (65/35, v/v, 15 ml) (Behar et al., 1989; Letellier et al*.* 1999). The aromatic fractions were finally re-concentrated to about 100 µl in HPLC grade Iso-octane (99% extra pure, Scharlau, ICS, St Medard en Jalles, France) and analyzed using GC-MS.

Samples analysis

Analyses were performed using HP 5980 series II gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) equipped with a splitless injector (purge delay 1 min, purge flow 60 ml min⁻¹). The injector was maintained at 270 C. The capillary column was coated with DB5 stationary phase (JW, Folson, CA, USA): 30 m x 0.25 mm ID x0.25µm film thickness. The temperature program used was 50 C (2 min) to 290 C (20 min) at 5 C min-.

Helium flowing at a constant flow rate of 1 ml min⁻¹ was used as a carrier gas. Gas chromatograph was coupled with an HP 5972 mass selective detector (electronic impact: 70 eV, voltage: 2000 V) operated under the single ion monitoring mode using the molecular ion of each compound at 1.23 scan $s⁻¹$ with the interface temperature of 290 C. PAHs were quantified relative to per-deuterated added to the freeze-dried samples prior to the extraction. The response factors of the different compounds were measured by injecting a solution of PAH mix 45 solution (Cluzeau info Labo, CIL) spiked with per-deuterated PAHs used to spike the samples.

All laboratory glassware and reagent containers were thoroughly cleaned and dried in an oven for 4 hours at 450 C. All reagents, solvents and standards were of HPLC quality, and tested for their suitability before sample analysis. Milli-Q water (organic grade quality) was used for all cleaning throughout the analytical process. Blanks accompanied batches of samples and run at the same time, under the same conditions.

GC-MS response factors obtained were between 0.84 to 1.41 showing that the equipment was fit to perform the analysis. The detection limits for all the PAHs were about 300pg injected which means about 5pg/g for each PAH in the sediment samples. The recoveries of Phenanthrene d_{10} , benzo[a]pyrene- d_{12} , benzo[e]pyrene- d_{12} and benzo [g, h, i] perylene-d₁₂, Fluoranthene-d₁₀, chrysene-d₁₂ and pyrene-d₁₀) were within the acceptable levels (98 -122%). The reproducibility was evaluated using SRM 1941a. The recoveries were >75% with a high precision.

Grain size and carbon analysis

Grain size was analyzed through sieving method. Total organic matter was analyzed through ashing method

while Total organic carbon (TOC) was determined following dichromate redox colorimetric method (Heanes 1984).

Data treatment and analysis

PAHs data are represented as the concentration of each isomer and as the sums of all the isomers in each station. To test whether there were differences in PAHs concentration for the various stations sampled $(H_0:$ Stations had similar distribution of PAHs), the data was first subjected to Kolmogorov-Smirnov goodness of fit test for normality. The P<0.05 indicating that the samples were from populations with different distributions. This allowed for the use of a two-way ANOVA for significant difference testing. Pearson product- moment correlation was used to determine any relationships between PAH and grain size, organic matter and organic carbon.

RESULTS AND DISCUSSION

Particle size, organic matter and TOC concentration in the samples are shown in Table 1. TOC in the samples had a mean of 8.80 mg g^{-1} in Sabaki with Sabaki bridge having the highest concentration of 16.30 mg g^{-1} and a mean of 11.61 mg g^{-1} in Tana with Tana mouth having the highest concentration of 14.91 mg $g⁻¹$. Organic matter had a mean of 0.77 in Sabaki with the highest in Sabaki bridge 1.45 and river Tana had a mean of 4.16 with the highest in Tana 3 with 8.02.Percentage sediment particle size < 63µm had a mean of 39.80 in Sabaki river with the highest in bridge. The correlation analysis of PAH against TOC, particle size and organic matter were not significant an indication that these parameter didn't influence PAH concentration in these estuaries.

PAHs concentration, composition and distribution

The concentration of PAH isomers for each sample are given in Table 2. The total PAH contents in sediments of Kenyan estuaries ranged from 0.33 ng g 1 dw at Ramisi Mouth Station to 13.20 ng g⁻¹ dw at Tana 2 Station (Table 2) with an overall mean of 4.44 ng g^1 for all the stations. The mean total PAH content in Ramisi, Sabaki and Tana estuaries were 0.33, 2.11 and 7.22 ng g^{-1} respectively showing that the total PAH content was generally higher in Tana estuary as compared to Sabaki and Ramisi estuaries. This study confirms the results of the previous study by Mohammed et al. (2002) which reported that PAHs have a global distribution from inland lakes and urban rivers to the open ocean with a wide range of concentrations.

The higher mean total PAH content in Tana and Sabaki estuaries as compared to Ramisi estuary could be

Table 1. TOC concentration (mg/g), organic matter (%) and <63 particles fraction (%) in sediment from Kenyan estuaries.

| STN | PAH (ng/g) | TOC (mq/q) | organic matter % | \leq 63µm particles fraction (%) |
|---------------|--------------|------------|------------------|------------------------------------|
| Ramisi Mouth | 0.33 | 13.36 | 0.76 | 0.10 |
| Sabaki mouth | 0.88 | 3.45 | 0.14 | 5.54 |
| Sabaki Upper | 1.66 | 6.64 | 0.72 | 35.21 |
| Sabaki bridge | 3.78 | 16.30 | 1.45 | 78.65 |
| Tana Mouth 1 | 0.78 | 14.91 | 1.02 | 4.09 |
| Tana 4 | 7.44 | 13.45 | 4.67 | 37.26 |
| Tana 3 | 7.47 | 6.18 | 8.02 | 35.93 |
| Tana 2 | 13.20 | 11.92 | 2.92 | 41.12 |

Table 2. Concentration of PAHs in surface sediment from selected Kenyan estuaries (ng g⁻¹ dw)

∑PAHs: the sum of seventeen priority PAHs; ND: Not detected, assuming that the values of different congeners less than ND are equal to 0.

attributed to the rapid urbanization and industrialization and high erosion activities in their catchment areas. Even though Tana and Sabaki systems showed a relatively higher concentration of total PAH, it is worth noting that the most seaward stations for both the estuaries (Sabaki mouth and Tana mouth) showed very low concentration as compared to the upstream stations sampled. This shows that even though PAHs may enter the estuarine waters through shipping activities and transport as well as accidental sea oil spills, the PAH in these systems were basically river derived with a terrestrial input.

A highly significant difference was observed in PAHs concentration in sediments from the different sampling sites (F=8.55; P ˂0.01). The high levels of total PAHs content in Tana 1, 2, 3, Sabaki upper and Sabaki bridge stations as compared to the other stations could have resulted from pollution from the rivers' upstream areas. One source of PAH to the rivers is sewage input, that is discharged at various points along these rivers. The contribution of sewage discharge to higher total PAH content of sediments has also been reported in Yangtze River Estuary by Liu et al. 2001.

Most of the individual PAH compounds were detected at all of the stations even though many of these compounds were only present at concentrations less than 1 ng g^1 (Table 2). The PAH distribution profiles in sediment samples were dominated by 2- and 3-ring PAHs (Light Molecule Weight- LMW). Occasionally, the 4, 5 or 6-ring HMW PAHs were also relatively more abundant especially for Tana 3 and 4 (Figure 2). The importance of LMW PAHs has frequently been noted in the literature for sediments from river, marine or lacustrine environments (Doong and Lin 2004; Luo et al. 2006). The predominance of LMW PAHs is indicative of a recent input of PAHs into Kenyan estuarine sediment because 2- and 3-ring PAHs strongly adsorb onto the

Sampling Station

Figure 2. Relative contribution of the individual PAHs in the various sampling sites.

surface of fine particles. Atmospheric fallout could also have led to the relatively high abundances of LMW PAHs in the Kenyan estuaries.

The levels of total PAHs in Kenyan Estuaries were found to be extremely low in comparison to the other highly urbanized and contaminated estuaries in the world (Table 3). The low concentrations of PAHs in Kenyan estuarine sediments are probably due to less anthropogenic activities in the catchment and riparian areas of these estuaries. The low levels could also be as a result of increased dilution of sedimentary PAHs due to excessive sediment load from anthropogenic activities and river-borne suspended particles caused by surface runoffs during heavy and frequent down-pours.

PAH sources identification

Parent and alkyl-substituted PAHs of both natural and anthropogenic sources are introduced into the environment mainly via industrial discharge (Simpson et al., 1996), spillage of petroleum/ fossil fuel (Pettersen et al., 1997; Wang et al., 1999), fossil fuel combustion and automobile exhaust, as well as via non-point sources such as urban runoff and atmospheric fallout (Simck et al., 1996). Since PAH compositions of the two sources frequently overlap, the significance of anthropogenic PAH in the environment has in the past been evaluated

against a dynamic background of natural PAHs.

A number of authors (e.g. Tsapakis et al., 2003; Yunker et al., 2002; Zhang et al., 2004) have used PAH molecular ratios, such as anthracene/anthracene + phenanthrene(Ant/Ant+Phe),benzo(a)anthracene/benzo (a)anthracene+chrysene(BaA/BaA+CHR),fluoranthene/flu oran thene+pyrene (Fl/Fl+Pyr) and ideno(1,2,3 cd)pyrene/ideno (1,2,3cd) pyrene+benzo(ghi) pery-lene (IP/IP+BghiP), as distinct chemical tracers to determine possible sources of PAHs. For this study, fluoranthene/fluoranthene+pyrene (Fl/Fl+Pyr) ratio was used to determine the sources of PAH. An Fl/Fl+Pyr ratio of < 0.4 implied petroleum source, 0.4 to 0.5 implied petroleum combustion, and > 0.5 implied combustion of coal and biomass sources (Doong and Lin 2004;Yunker et al., 2002). The Fl/Fl+Pyr isomer ratios showed that PAHs in Kenyan estuarine sediments were derived primarily from petroleum sources apart from Sabaki Bridge station whose PAH were found to be from both petroleum and petroleum combustion sources (Figure 3).

Sabaki Bridge could have received quite a substantial amount of PAHs from the traffic through street dust. The contribution of street dust (with the spilled oil) to sedimentary PAHs has been the subject of many studies (Takada et al., 1991; Su et al., 2000*;* VanMetre et al., 2000). Street dust is normally transported into the river via street runoff and could be an important source of PAHs in the bridges. PAHs originating from

Table 3. Comparison of total PAH (ng g⁻¹) in sediments from different locations in the world.

Sampling Station

Figure 3. Comparison of FI/FI+Pyr PAH molecular ratio for the studied estuaries.

anthropogenic sources, such as combustion of fossil fuels and direct release of oil products have also been reported elsewhere by Simpson et al., (1996). The high levels of PAH of petroleum combustion sources at Sabaki Bridge confirms that atmospheric particle emission and fallout might be another important route for deposition of PAHs in this station.

The sediments studied exhibited evidence of petroleum derived pollution. This was likely caused by leakage of oil from agricultural machine and discharge and careless handling of used oils by the mechanics and garages. Frequent and strong rains in the catchment of these rivers may have contributed to continuous and extensive washing and transport of these spilled petroleum PAHs

from land to the rivers and coastal zones. Once the PAHs were introduced into the estuarine environment, they rapidly adsorbed onto suspended particles and hence bottom sediments due to their hydrophobic nature (Nogami et al., 2002; Tam et al., 2001) which could have led to their accumulation in the sediments.

Even though the frequent heavy rain in the catchment with the fast flushing capability could have transferred PAHs to the rivers before they underwent various removal processes in terrestrial environments (such as photo degradation, blowing away and atmospheric transport of particulate PAHs by wind and in-river degradation), the heavy rains could have also led to surface erosion contributing large amounts of soils to the rivers thus diluting PAHs in the some stations.

PAHs in sediments collected from Sabaki Mouth and Tana Mouth had petrogenic signature, indicating they are heavily impacted by petrogenic input whereas Tana 4 Station showed a pyrogenic signature. Normally, petrogenic-source PAHs (e.g., crude and fuel oil) contain LMW PAHs with a severe depletion of HMW PAHs, while pyrogenic sources are abundant in HMW PAHs. Ramisi Mouth, Sabaki Bridge, Tana 1 and Tana 2 contained considerable amounts of both HMW PAHs and LMW PAHs, indicating the input of both petrogenic and pyrogenic sources.

Ecotoxicological significance

PAHs toxicity to aquatic organisms has been reported by a number of authors e.g. Boxall and Maltby (1997), with some PAHs exhibiting carcinogenic or mutagenic effects (Chen et al., 2006). Some of the PAHs (i.e. BaA, BbF, BkF, BaP), which are known to be carcinogenic to mammals, were found in the Kenyan estuaries sediments. In order to assess sediment quality, PAH levels in sediment were compared with effects-based sediment quality guideline values (Long et al., 1995). Concentration of both individual and total PAHs were all significantly lower than the Effects Range Low (ERL) level of 4000 ng g^{-1} dw proposed as the Sediment Quality Guidelines (SQGs) for marine ecosystems by Long et al., (1995). Even though biological toxic effects of PAHs in Kenyan estuaries may exist, such effects are not expected to be significant in the short term unless the levels of PAHs loading in the sediments increase significantly.

Conclusion and recommendations

1. PAHs composition in the four estuaries comprised mainly of 2- and 3-ringed PAHs. This indicates a relatively recent local source of PAHs. Diagnostic ratios analysis identified anthropogenic activities as the main sources of PAHs in sediments.

2. Run-off of used oil and combustion residues from roads as a significant source of pyrogenically derived PAHs to receiving waters was confirmed by the results of this study which showed high concentrations of petroleum derived PAHs in most samples and combustion derived PAHs in sediments at Sabaki Bridge. Road traffic and industrialization is predicted to increase considerably in the near future and this may result into a potential increase in the magnitude of inputs of PAHs to the receiving waters from this source. This study recommends the introduction of appropriate highway drainage systems to control and reduce inputs of PAHs and other contaminants to the receiving waters. These systems could include but not be limited to gully systems, surface water channels and ditches which can divert and collect runoff for treatment or disposal (CIRIA 1994).

3. Unlike in developed countries with stringent laws and enforcement mechanism and organized oil recycling mechanisms with a high degree of willingness to participate in recycling programs (Latimer et al., 1990), Kenya has no recycling program for used oil nor does a law guiding the disposal of used oil exist. Most of the used oils are improperly stored, allowing for indiscriminate spillage and many a time are directly disposed of into the drains. Heavy rains that occur almost every day in the catchment areas of these rivers can easily wash the spilled oil into the rivers, and estuaries without allowing adequate time to undergo degradation on the ground or to receive clean-up activities. We therefore recommend formulation of laws and regulations to guide the handling and disposal of oil. We also recommend sensitization of the general public on the effects of oil in the environment and the need to recycle oil.

REFERENCES

- Behar F, Leblond C, Saint-Paul C (1989). Analyse quantitative des effluents de pyrolyse en milieu ouvert et ferme. Oil Gas Sci. Technol., 44: 387-411.
- Boxall ABA, Maltby L (1997). The effects of motorway runoff on freshwater ecosystems: 3. Toxicant conformation. Arch. Environ. Con. Tox. 33:9-16.
- Chen SJ, Luo XJ, Mai BX, Sheng GY, Fu JM , Zeng E(2006). Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the Northern South China Sea. Environ. Sci. Technol., 40: 709-714.
- CIRIA (1994). Control of pollution from highway drainage discharges. Report No. 142. London: CIRIA.
- Daisy BH, Strobel GA, Castillo U, Ezra D, Sears J, Weaver DK , Runyon JB(2002). Naphthalene, an insect repellent, is produced by Muscodor vitigenus, a novel endophytic fungus. Microbiol., 148: 3737-3741.
- Doong R, Lin YT (2004). Characterization and distribution

of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan. Wat. Res., 38: 1733-1744.

- Guo J, Wu F, Luo X, Liang Z, Liao H, Zhang R, Li W, Zhao X, Chen S, Mai, B(2010). Anthropogenic input of polycyclic aromatic hydrocarbons into five lakes in Western China. Environ. Pol., 158: 2175-2180.
- Heanes DL (1984). Determination of total organic c in soils by improved chromic acid digestion and spectrophotometric procedure. Commun Soil Sci. Plan, 15: 1191-1213.
- Katayama A, Bhula R, Burns GR, Carazo E, Felsor A, Hamilton D, Harris C, Kim YH, Kleter G, Koerdel W, Linders J, Peijnenburg JGMW, Sabijic A, Stephenson RG, Racke D K, Rubin B, Tanaka K, Unsworth J, Wauchope RD (2010). Bioavailability of xenobiotics in the soil environment. Rev. Environ. Contam., 203: 1-86.
- Kim EJ, Oh JE, Chang YS (2003). Effects of forest fire on the level and distribution of PCDD/Fs and PAHs in soil*.* Sci. Total Environ., 311: 177-189.
- Latimer JS, Hoffman EJ, Hoffman G, Fasching JL, Quinn JG. 1990. Sources of petroleum hydrocarbons in urban runoff. Water Air Soil Poll., 52:1-21.
- Letellier M, Budzinski H, Bellocq J, Connan J (1999). Focused microwave-assisted extraction of polycyclic aromatic hydrocarbons and alkanes from sediments and source rocks. Org. Geochem. 30: 1353-1365.
- Liu M, Hou L J, Yang Y, Zou H X, Lu J H , Wang X R (2001). Distribution and sources of polycyclic aromatic hydrocarbons in intertidal flat surface sediments from Yangtze Estuary, China. Environ. Geochem., 41: 90- 95.
- Long ER, MacDonald DD, Smith SL, Calder FD (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage., 19: 81-97.
- Luo XJ, Chen SJ, Mai BX, Yang QS, Sheng GY, Fu JM (2006). Polycyclic aromatic hydrocarbons in suspended particulate matter and sediments from the Pearl River Estuary and adjacent coastal areas, China. Environ. Pollut., 139: 9-20.
- Meharg AA, Wright J, Dyke H, Osborn D (1998). Polycyclic aromatic hydrocarbon (PAH) dispersion and deposition to vegetation and soil following a large-scale chemical fire. Environ. Pollut. 99: 29-36.
- Nadal M, Schuhmacher M, Domingo JL (2004). Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. Environ. Pollut., 132: 1-11.
- Nogami Y, Imaeda R, Ito T, Kira, S (2002). Benzo (a) pyrene adsorbed to suspended solids in fresh water. Environ. Toxicol., 15: 500-503.
- Ongwenyi GS, Denga FGO, Abwao P, Kitheka JU (1993). Impacts of floods and drought on the development of water resources of Kenya: case studies of the Nyando and Tana catchments. IAHS-AISH P 216: 117-123.
- Patrolecco L, Ademollo N, Capri S, Pagnotta R, Polesello S (2010). Occurrence of priority hazardous PAHs in

water, suspended particulate matter, sediment and common eels (Anguilla Anguilla) in the urban stretch of the River Tiber, Italy. Chemo., 81:1386-1392.

- Pettersen H, Näf C, Broman D (1997). Impact of PAH outlets from an oil refinery on the receiving water areasediment trap fluxes and multivariate statistical analysis. Mar. Pollut. Bull. 34: 85-95.
- Qiao M, Wang C, Huang S, Wang D, Wang Z (2006). Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. Environ. Int., 32: 28- 33.
- Qin Y, Zheng B, Lei K, Lin T, Hu L, Guo Z (2011). Distribution and mass inventory of polycyclic aromatic hydrocarbons in the sediments of the south Bohai Sea, China. Mar. Pollut. Bull. *62*: 371-376.
- Saha SK (1982). Irrigation planning in the Tana Basin of Kenya. Water Supply Manage 6: 261-279.
- Simck MF, Eisenreich SJ, Golden KA, Liu S, Lipiatou E, Swackhamer DL, Long DT (1996). Atmospheric loading of polycyclic aromatic hydrocarbons to Lake Michigan as recorded in the sediments. Environ. Sci. Technol. 30: 3039-3046.
- Simpson CD, Mosi AA, Cullen WR, Reimer KJ (1996). Composition and distribution of polycyclic aromatic hydrocarbons in surficial marine sediments from Kitimat Harbour, Canada. Sci. Total Environ., 181: 265-278.
- Su MC, Christensen ER, Karls JF, Kosuru S, Imamoglu I (2000). Apportionment of polycyclic aromatic hydrocarbon sources in lower Fox River, USA, sediments by a chemical mass balance model. Environ. Toxico.l Chem. 19: 1481-1490.
- Takada H, Onda T, Harada M, Ogura N (1991). Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in street dust from the Tokyo Metropolitan area. Sci. Total Environ. 107: 45.
- Tam NFY, Ke L, Wang XH, Wong YS (2001) .Contamination of polycyclic aromatic hydrocarbons in surface sediments of mangrove swamps. Environ. Pollut., 114:255-263.
- Tang L, Tang XY, Zhu YG, Zheng MH, Miao QL (2005). Contamination of polycyclic aromatic hydrocarbons (PAHs) in urban soils in Beijing, China. Environ. Int. 31: 822-828.
- Tsapakis M, Stephanou E G, Karakassis I (2003). Evaluation of atmospheric transport as a nonpoint source of polycyclic aromatic hydrocarbons in marine sediments of the Eastern Mediterranean. Mar. Chem. 80: 283-298.
- VanMetre PC, Mahler BJ, Furlong ET (2000). A Simplified Approach for Monitoring Hydrophobic Organic Contaminants Associated with Suspended Sediment: Methodology and Applications. Environ. Sci. Technol. 44: 88-297.
- Venkatesan MI (1988). Occurrence and possible sources of perylene in marine sediments- a review. Mar. Chem. 25: 1-27.

Wang ZD, Fingas M, Page DS (1999). Oil spill identification. J Chromatogr. A 843: 69-411.

- Wilcke W, Amelung W, Martius C, Garcia VB, Zech W (2000). Biological sources of polycyclic aromatic hydrocarbons (PAHs) in the Amazonian rain forest. J Plant Nutr. Soil Sc. 163: 27-30.
- Wilcke W, Zech W, Kobza J (1996). PAH pools in soils along a PAH gradient. Environ. Pollut. 92: 307-313.
- Wilcke W (2007). Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. Geoderma. 141: 157-166.
- 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 as

indicators of PAH source and composition. Org. Geochem., 33 489-515.

- Zakaria MP, Takada H, Tsutsumi S, Ohno K, Yayamada J, Kouno E, Kumata H (2002). Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs. Environ. Sci. Technol., 36: 1907- 1918.
- Zhang ZL, Huang J, Yu G, Hong HS (2004). Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environ. Pollut., 130 249-26.