

## DETERMINATION OF PAHs IN MARINE SEDIMENTS: ANALYTICAL METHODS AND ENVIRONMENTAL CONCERNS

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### ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) are one of the major categories of pollutants entering the marine environment and finally accumulating in the sediments. Their occurrence raises major concerns for human health, especially during coastal activities (bathing waters, aquaculture, etc), having combined adverse effects still largely unknown when they are present as mixtures. Moreover, during their remobilization (e.g. dredging activities), their bioavailability can increase resulting in a risk for marine environment. Several of them are known to be potential human carcinogens including benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene and benzo[ghi]perylene. Therefore they have been included in the priority list of the Water Framework Directive 2000/60/EC and also sixteen of them have been regulated by the US EPA as priority pollutants, and their distributions in the environment and potential human health risks have become the focus of much attention.

The determination of PAHs in environmental matrices has been subject of great scientific attention during the latest years, as the accuracy and sensitivity of analytical methods need to be improved in order to be able to detect the compounds of interest in a complex matrix such as sediments. Therefore, significant research is being devoted to the optimization of analytical methodologies. A great number of studies have been performed on PAHs analysis in marine sediments. Various analytical procedures based on gas chromatographic analyses are reviewed and comparatively discussed in this paper.

**KEYWORDS:** Polycyclic aromatic hydrocarbons, marine sediment pollution, environmental analysis.

### 1. INTRODUCTION

Marine sediments consist an important source of information regarding the human activities in the coastal area as well as the fate of xenobiotics during long-term time intervals. Although no relevant regulation has been established, the monitoring of pollutants in sediments can provide information for the assessment of the potential toxic effects of these compounds as well as for the support of decision-making from management authorities. The scientific interest in the sector of marine sediments quality is quite recent and has increased especially during the last ten years in relation to the application of the Water Framework Directive 2000/60/EC (WFD 2000; Naddeo *et al.*, 2005; Hadjibiros, 2005; Arsene *et al.*, 2009; Aloupi *et al.*, 2007; Demetriou, 2004; Mylopoulos *et al.*, 2008; Ma *et al.*, 2008).

The Water Framework Directive 2000/60/EC set the aim of the achievement and preservation of the "Good Ecological Status" of the waters – surface waters, groundwaters and coastal

waters – of the EU member states until 2015, while in parallel the monitoring of their quality is required. In contrast to other types of water, coastal waters consist a particular matrix with specific properties due to their salinity and the particulate organic matter contained in them. In coastal areas affected by various human activities, the effects have already become obvious, having social, economic and environmental impacts (Boonyatumanond *et al.*, 2006; Filipkowska *et al.*, 2005; Kwon *et al.*, 2000). The quality of marine waters is directly related to the quality of sediments, because they are the final compartment of storage of a large number of xenobiotics.

Marine pollution in coastal areas is a subject of global interest, due to the large number of toxic substances transported from human activities (Filipkowska *et al.*, 2005; Vagi *et al.*, 2005; Lors *et al.*, 2009). Industrialization and urbanization have been developed traditionally in the coastal areas, including the development of large metropolises, harbours and industrial and shing bases, resulting in the deterioration of neighboring marine environments. Among a long list of various contaminants, Polycyclic Aromatic Hydrocarbons (PAHs) constitute a major environmental concern on marine ecosystems because of their adverse health effects on organisms, including endocrine disrupting activity (Kanaki *et al.*, 2007, Zaghden *et al.*, 2007; Catsiki *et al.*, 2003). Some of them are carcinogenic and are on the USEPA list of priority pollutants. According to the Water Framework Directive 2000/60/EC, these substances are considered as priority substances due to their environmental behaviour and their toxic effects. They are characterized by high toxicity, high stability in the environment and high lipophilicity, resulting in their transport through the trophic chain with final destination the human organism (IARC, 1983; Okay *et al.*, 2000; Vagi *et al.*, 2005).

The EU Directive 98/83/EC relevant to the water intended for human consumption, has set a limit of  $0.10 \mu\text{g l}^{-1}$  for the sum concentration of the compounds benzo-b-fluoranthene, benzo-l-fluoranthene, benzo-ghi-perylene and indeno-123cd-pyrene, while in the decision 2455/2001/EC for the establishment of a list of priority substances of the WFD 2000, PAHs have been included in this list and regulatory limits are to be set for inland, transitional and coastal waters. However, no limits have been set yet for marine sediments, although they are the final receivers of PAHs existing in the marine environment.

The introduction of PAHs in the marine environment is performed via processes such as the combustion of organic matter (pyrolytic origin), the slow transformation of organic matter in geothermal scale (petroleum hydrocarbons), and degradation of biogenic material (diagenesis). The naturally formed PAHs are biosynthesis products or come from oil upwelling and occur in the marine sediments at very low levels ranging from  $0.01$  to  $1 \text{ ng g}^{-1}$  dry weight (background concentrations). On the contrary, human activities are sources of a number of PAHs in the aqueous environment with the highest values being recorded in estuaries and coastal areas, as well as in areas with intense vessels transport and oil treatment. Some of them are considered potentially carcinogenic for human, in particular benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene and benzo[ghi]perylene (Anyakora *et al.*, 2005).

The development and optimization of analytical methods for the determination of priority substances in marine sediments is still in progress as analysis performance is directed towards optimum resolution of analytes, limit of detection, cleanup of environmental samples, etc (Abalos *et al.*, 1997; Ferguson *et al.*, 2001; Petrovic *et al.*, 2002; Shang *et al.*, 1999; Lekkas *et al.*, 2003; Andrzejewski and Nawrocki, 2005; Cancho and Ventura, 2005; Lekkas *et al.*, 2009). Marine sediments are a complex matrix for the determination of PAHs and other priority substances at trace concentration levels. The increase of sensitivity and recovery of analytical methods for their determination still consists a challenge for researchers worldwide, although there has been a great progress regarding the capabilities of the analytical instrumentation available nowadays. Many analytical methods have been developed, optimized and applied for the determination of PAHs in marine sediments (Anyakora *et al.*, 2005; Bartolomeè *et al.*, 2005; Brion *et al.*, 2005; Boonyatumanond *et al.*, 2006; Buseti *et al.*, 2006; Capelo *et al.*, 2005; Coartazar *et al.*, 2002; Culotta *et al.*, 2006; Fang *et al.*, 2005, 2006; Filipkowska *et al.*, 2005; Gimeno *et al.*, 2003; Kim *et al.*, 2003; Libando *et al.*, 2004; Liguori *et al.*, 2006; Olivella *et al.*, 2006; Pino *et al.*, 2001, 2003; Planas *et al.*, 2006; Popp *et*

*al.*, 2000; Quiao *et al.*, 2005; Ricardo *et al.*, 2005; Ricking *et al.*, 2002; Ruus *et al.*, 2005; Swindell *et al.*, 2006; Wu *et al.*, 2003).

It is well known that contamination sites raise significant environmental hazards for terrestrial and aquatic ecosystems. The USEPA has determined that contaminated sediments pose both ecological and human health risks throughout the United States. It is estimated that roughly 10% of the sediments from the nation's lakes, rivers and bays are contaminated with toxic chemicals that can adversely affect aquatic organisms or impair the health of humans or wildlife, who consume contaminated fish or shellfish (ATSDR, 1995; USEPA, 1993, 1994). They are important sources of pollution and may result in ecotoxicological effects, which can occur at all levels of the biological organization, from the molecular to the ecosystem level (Wernersson *et al.*, 2004; Fent, 2003; Del Valls *et al.*, 2002). Moreover, remobilization of toxic pollutants, thus increase of their bioavailability, can occur when contaminated sediments are disturbed and dredged (Water Framework Directive, 2000; Eggleton and Thomas, 2004).

## 2. GENERAL CHARACTERISTICS AND PROPERTIES OF PAHs

PAHs are organic compounds containing condensed aromatic rings in their molecules. The number and position of the rings as well as the number, position and nature of the atoms that can be present in the molecule affect the physical and chemical properties of PAHs, their environmental behavior and their interactions with biota and human.

Table 1 presents the basic physical and chemical characteristics for the PAHs most frequently detected in environmental matrices. PAHs have high melting and boiling points and low water solubilities. Their solubility in water decreases, while correspondingly their boiling and melting point increases, with increasing molecular weight (Albers, 1995). For example naphthalene (MW=128) has a water solubility value of  $31 \mu\text{g l}^{-1}$ , melting point  $80.5^{\circ}\text{C}$  and boiling point  $218^{\circ}\text{C}$ , while chrysene (MW=228) has water solubility  $0.006 \mu\text{g l}^{-1}$  melting point  $255^{\circ}\text{C}$  and boiling point  $448^{\circ}\text{C}$ .

Since the end of the 18<sup>th</sup> century, the relationship between exposure to PAHs and skin cancer was observed in chimneysweepers in England. Afterwards, many PAHs were recognized as carcinogens and mutagens. Toxicity tests such as Ames test have been applied to determine the toxicity of PAHs. It has been proved that some of them induce skin cancer and there are suspicions that some PAHs may induce lung cancer. However, carcinogenic activity is observed only after exposure to high concentrations for a long time. Experiments with animals have shown that the active dosages of PAHs are at least 1000 times higher than their daily intake by human with food and water. The daily intake of benzo[a]pyrene via a normal food and water consumption ranges between 0.5 and 2.5  $\mu\text{g}$  and very rarely exceeds 3 $\mu\text{g}$  (Kanaki, 2005). Although teratogenic action of some PAHs has been observed in animals, no similar action has been observed for humans. Their toxicity for aqueous plants ranges depending on the kind of the plant and the environmental conditions. PAHs did not show toxicity on fish unless they are exposed to high concentrations for long time intervals. Long-term exposure to high concentrations of PAHs can result in decrease of growth and of reproduction capability of various species. Moreover, abnormalities such as liver tumours, kidney problems have been reported. Table 2 summarizes the carcinogenic action of PAHs (Kanaki, 2005).

US EPA and others have developed a relative potency estimate approach for the PAHs (EPA, 1993). By using this approach, the cancer potency of the other carcinogenic PAHs can be estimated based on their relative potency to benzo[a]pyrene. The toxicity equivalence factors (based on carcinogenicity) calculated for PAHs (Table 2.) USEPA has performed weight of evidence evaluations of several of the PAHs discussed in this profile. The carcinogenicity classifications currently verified by EPA's Carcinogenicity Risk Assessment Verification Endeavor Work Group (EPA, 1994) which are listed in Table 2 also.

Table 1. Physical and chemical characteristics of selected PAHs  
(Adopted from ATDSR, 1995)

Characteristics	Formula	Molecular weight	Melting point (°C)	Boiling Point (°C)	Water solubility (g 100ml <sup>-1</sup> )	log K <sub>ow</sub>	Vapore pressure (mmHg)
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	178.233	99.5	340	1.18 x 10 <sup>-4</sup>	4.45	
Fluoranthene	C <sub>16</sub> H <sub>12</sub>	202.255	110.8	375	2.65x10 <sup>-5</sup>	4.90	5.0×10 <sup>-6**</sup>
Pyrene	C <sub>16</sub> H <sub>10</sub>	202.255	156	404	1.3x10 <sup>-6</sup>	4.88	2.5×10 <sup>-6**</sup>
Benzo [a]anthracene	C <sub>18</sub> H <sub>12</sub>	228.2928	159.8	437.6	1.4x10 <sup>-6</sup>	5.61	2.2×10 <sup>-8*</sup>
Benzo [b] fluoroanthene	C <sub>20</sub> H <sub>12</sub>	252.3148	167	357	1.2x10 <sup>-7</sup>	6.04	5.0×10 <sup>-7*</sup>
Benzo [k] fluoroanthene	C <sub>20</sub> H <sub>12</sub>	252.3148	215.7	480	5.5x10 <sup>-8</sup>	6.06	9.59×10 <sup>-11</sup>
Benzo [e] pyrene	C <sub>20</sub> H <sub>12</sub>	252.3148	178	492	<0.1		5.6×10 <sup>-9**</sup>
Indeno [1,2,3] cd pyrene	C <sub>22</sub> H <sub>12</sub>	276.3368	162.5	536	6.2x10 <sup>-6</sup>	6.58	10 <sup>-11</sup> ×10 <sup>-6*</sup>
Benzo [g,h,i] perylene	C <sub>22</sub> H <sub>12</sub>	276.3368	278.3	500	2.6x10 <sup>-8</sup>	6.50	1.03×10 <sup>-10**</sup>
Dibenzo [a,h] anthracene	C <sub>22</sub> H <sub>14</sub>	278.3526	266	524	5x10 <sup>-8</sup>	6.84	1.0×10 <sup>-10*</sup>

\* at 20°C ; \*\* at 25°C

Table 2. Carcinogenic action of PAHs (Kanaki, 2005)

PAHs	Indicator of carcinogenesis <sup>1</sup>	Total estimation <sup>2</sup>	EPA Classification (EPA, 1994) <sup>3</sup>	Toxicity Equivalence Factor (TEF) (EPA; 1993)
Acenaphthylene			D	0.001
Anthracene	I	3	D	0.01
Benzo[a]anthracene	S	2A	B2	0.1
Benzo[b]fluoranthene	S	2B	B2	0.1
Benzo[k]fluoranthene	S	2B	B2	0.1
Benzo[b]fluorene	I	3		
Benzo[g,h,i]perylene	I	3	D	0.01
Benzo[a]pyrene	S	2A	B2	1
Benzo[e]pyrene	I	3		
Chrysene	L	3	B2	0.01
Fluoranthene	I	3	D	0.001
Fluorene	I	3	D	0.001
Indeno[1,2,3-c,d]pyrene	S	2B	B2	0.1
Perylene	I	3		
Phenanthrene	I	3	D	0.001
Pyrene	I	3	D	0.001
Dibenzo[a,h]anthracene	S	2A	B2	5
Dibenzo[a,h]pyrene	S	2B		
Benzo[c]fluorene	I	3		
Benzo[j]fluoranthene	S	2B		
Dibenzo[a,e]pyrene	S	2B		

<sup>1</sup> No adequate data for humans. For animals: I, insufficient data; L, limited data; S, sufficient data

<sup>2</sup> 1, carcinogen for humans; 2A, probable carcinogen for humans; 2B, possible carcinogen for humans; 3, not classified regarding carcinogenicity for humans

<sup>3</sup> D: not classifiable as to human carcinogenicity; B2: probable human carcinogen

### 3. SOURCES AND FATE OF PAHs IN THE MARINE ENVIRONMENT

PAHs originate from anthropogenic sources such as industrial production, transportation and waste incineration as well as incomplete combustion processes such as forest fires and volcanic eruptions. However the production from natural processes is generally low compared to those from anthropogenic sources. Zaghden *et al.* (2007) classified three categories: petrogenic origin, pyrolytic origin, natural oil seeps, diagenetic origin basing upon diagnostic ratios and/or predominance of different PAHs congeners (Sprovieri *et al.*, 2007). Petrogenic PAHs are related to petroleum, including crude oil and its refined products. Biogenic PAHs are generated by biologic processes or by early stages of diagenesis in marine sediments (e.g. perylene). Pyrogenic PAHs are generated by the combustion of fossil fuels (coal and oil) and of recent organic material such as wood (Planas *et al.*, 2006).

PAHs are widespread contaminants of the ocean (NRC, 2003). However their concentrations in sediments of coastal embayments, estuaries and continental shelves are often much higher due to greater pressures of specific anthropogenic inputs (Liu *et al.*, 2007), suggesting a direct influence of these sources on the pollutant distribution patterns (Sprovieri *et al.*, 2007). Due to the chemical composition of seawater, the occurrence of PAHs, which are very hydrophobic compounds, will range at very low concentration levels ( $< 1 \text{ ng l}^{-1}$ ), in contrast to other aqueous matrices such as wastewater, river water, rainwater and sediments, where the corresponding values range, depending on the study area, from  $1 \text{ ng g}^{-1}$  to or greater than  $100 \text{ ng g}^{-1}$  per dry weight (Filipkowska *et al.*, 2005; Kiss *et al.*, 1996). Due to their hydrophobic character, PAHs tend to adsorb onto the particulate matter resulting in their transport and accumulation in the sediments.

Moreover the processes of industrialization and urbanization which are stepping rapidly in countries like India and China increase the potential associated PAHs inputs (Xu *et al.*, 2007). Studies focused on the developing coastal regions heavily contaminated show that contamination level of those regions are growing in the range of other polluted industrialized zones of developed countries (Yim *et al.*, 2007).

Atmospheric deposition, river runoff, domestic and industrial outfalls and direct spillage of petroleum or petroleum products are the main routes that introduce anthropogenic PAHs in marine environment. The knowledge of sources and possible transport pathways in aquatic sediments is the first step for an effective pollution control (Li *et al.*, 2001). Vessels have a significant contribution by transporting these compounds in the marine environment. Especially in harbours, where the renewal of waters through contact with the open sea is limited, the accumulation of PAHs can be significant (Anyakora *et al.*, 2005; Bakker *et al.*, 2000, N'Guessan *et al.*, 2004).

Once introduced into the marine environment, physical transport and mechanical factors are most responsible for the observed distribution of PAHs in sediments (Yim *et al.*, 2007). They are present in both dissolved and particulate phases. Due to their low solubility and their hydrophobic nature they are easily associated with inorganic and organic suspended particles and may accumulate to high concentrations in sediments (Culotta *et al.*, 2006).

The final fate of PAH is generally sedimentary deposition, after transport in the water column, as reported for material collected in sediment traps (Zaghden *et al.*, 2007). However in situ factors as partitioning of PAHs between sorbed and aqueous phases, bioturbation and selective microbial degradation may affect the resultant observed PAHs composition and the absolute PAHs compounds (Yim *et al.*, 2007)

A major part of recent studies on hydrocarbon pollution focuses on the northwestern part of the Mediterranean Sea (Lipiatou *et al.*, 1997; Dachs *et al.*, 1999; Albaigés, 2005). But there is a remarkable lack of information regarding the eastern Mediterranean Sea (Gogou *et al.*, 2000) and the southern Mediterranean Sea, with scarce data for the Algerian coasts (Sellali *et al.*, 1992) and Egyptian coasts (Aboul-Kassim and Simoneit, 1995, 1996). It is urgent to better assess a budget of hydrocarbon contamination for the Med Sea. The major problem remains the lack of data for the southern and east Mediterranean Sea.

Sprovieri *et al.* (2007) surveyed the priority PAHs in surface sediment samples collected from the Naples harbour varying from 9 to  $31774 \text{ ng g}^{-1}$ . Three and four rings PAHs appeared dominant in the studied sediments with median concentration values generally higher than the 60–70% of the PAHs total concentrations. Neither grain size nor TOC were correlated with

the distribution of either PAHs or single congeners. The Naples harbour showed a median and a range of variability higher than most of other Mediterranean and European ports (Sardinia, Corsica, Spain, France and England) but similar to those measured in the USA, middle East and Australian commercial harbours. Total PAHs concentrations measured by Vane *et al.* (2007), in sediments from the Mersey Estuary (UK) ranged from 626 to 3766 mg kg<sup>-1</sup> intermediate in comparison to other U.K estuaries with similar histories of industrialisation and urbanisation. The molecular indices in this case suggested mainly pyrolytic inputs, augmented by a variety of industrial or petrogenic sources.

#### 4. ANALYTICAL METHODS FOR THE DETERMINATION OF PAHS IN MARINE SEDIMENTS

The most common technique utilized for the extraction of PAHs from sediments was initially Soxhlet extraction (Kennicutt *et al.*, 1990). However, more recently, alternative methods have been developed such as ultrasonic extraction, microwave dissolution, pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE), in order to reduce the volume of solvents used as well as the time required for analysis (Richter *et al.*, 1997; Berset *et al.*, 1999; Hawthorne *et al.*, 2000; Hubert *et al.*, 2000; Richter, 2000; Wennrich *et al.*, 2000; Wong and Wang, 2001). Solid phase microextraction (SPME) techniques have also started gaining interest for sediment samples. Pino *et al.* (2003) combined a micellar microwave-assisted extraction technique with SPME (micellar solid-phase microextraction, MSPME) to determine PAHs in a certified marine sediment (Pino *et al.*, 2003).

Because sediments are a complex substrate for analysis, different cleanup techniques have been developed in order to be applied after extraction to remove potential interferences and to clarify the final extracts prior to GC analysis. Such methods are solid phase extraction (SPE), HPLC cleanup, and column chromatography using a variety of adsorbents (e.g. acid and base modified silica gel, alumina, florisil). However, by use of these cleanup procedures, the analysis time and effort is again increased, therefore studies on the combination of extraction and cleanup procedures with automated sample handling devices have been reported (Kim *et al.*, 2003). Chemical modifiers such as Na<sub>4</sub>EDTA have also been utilized, aiming to increase the extraction efficiency for PAHs from sediments (Kim *et al.*, 2003).

Table 3 provides summary information on the analytical methods applied by different researchers and the analytical conditions used in each case as well as method validation results (recoveries and detection limits), and figure 1 presents a representative chromatogram obtained through GC-MS analysis of a marine sediment sample.

As it can be seen from Table 3, the chromatographic column HP-5 or equivalent is mostly used, by GC-MS analysis. Cleanup procedures are applied by many researchers in order to increase the sensitivity of the methods, usually by silica/alumina columns, and desulfurization by activated copper. Some studies still utilize the traditional time-consuming but effective Soxhlet extraction, while HPLC instrumentation is also used in some cases with relatively good results. It can be observed that the sample preparation step is often tedious, involving much time and effort, in order to obtain a clear extract for low-levels PAHs analysis, and this is due to the complexity of the sample matrix. Ultrasonic extraction appears to be the mostly preferred sample preparation method currently. Following the ongoing technological evolution in the laboratory equipment and consumables, the aim of tracing the PAHs residues in the marine sediments with higher precision and accuracy is being approached.

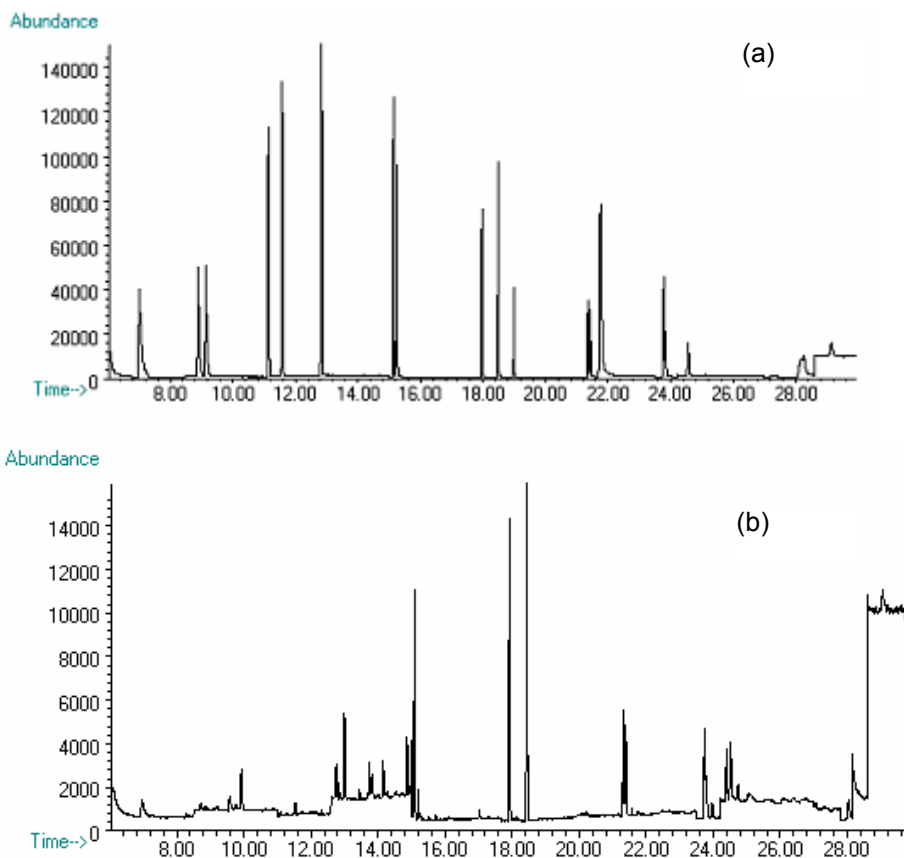


Figure 1. GC-MS chromatograms of priority PAHs (a) standard solution, (b) marine sediment sample from Mytilene port (Kostopoulou *et al.*, 2007)

## 5. CONCLUSION

Due to continuously increasing anthropogenic activities, the pollution of sediments in coastal areas is a subject taking more attention to handle. PAHs are characterized by high toxicity, high environmental stability and high hydrophobicity, resulting in their accumulation through the trophic chain with final destination the human body, and have been included in the priority substances of the Water Framework Directive. The distributions of PAHs in the environment and potential human health risks have become the focus of much attention. Their presence in marine sediments combined with other potentially toxic compounds can result in negative effects, which up to now have not been investigated to a large extent, mainly due to lack of appropriate methodology and the complexity of the subject matter. During the latest years, significant research is being devoted to the optimization of analytical methodologies for the determination of trace concentrations of PAHs in complex matrices such as sediments.

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Table 3. Analytical methods applied by different researchers for the determination of PAHs in marine sediment samples

PAHs studied	Sample preparation	Column and temperature program used	Recovery (%)	LOD
Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benz[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene Benzo[ghi]perylene, Dibenz[a,h]anthracene Indeno[1,2,3cd]pyrene (Reference: Anyakora <i>et al.</i> , 2006)	Soxhlet extraction with dichloromethane for 16 h	DB-5MS (70 °C for 4 min, 10 °C min <sup>-1</sup> to 300 °C, held for 10 min)	90-118	0.02-1.7 µg ml <sup>-1</sup>
Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzofluoranthene Benzo[e]pyrene Benzo[a]pyrene Perylene Indeno[1,2,3-cd]pyrene Benzo[ghi]perylene Coronene (Reference: Boonyatumanond <i>et al.</i> , 2006)	Pressurized solvent extraction with a mixture of dichloromethane and acetone (3:1, v/v) at 175 °C and 10.5 MPa for 5 min. Rotary preconcentration, cleanup with 5% H <sub>2</sub> O deactivated silica gel column, elution with eluted with 20 mL hexane/ dichloromethane (3:1, v/v). Activated copper treatment, pass through fully activated silica gel column, elution with hexane/dichloromethane (3:1, v/v).	HP5-MS (70 °C for 2 min, 30 °C min <sup>-1</sup> to 150 °C, increased to 310 °C at 4 °C min <sup>-1</sup> and held for 10 min)	75-105	1 ng g <sup>-1</sup>
Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a)anthracene Chrysene Benzo(b,k)fluoranthene Benzo(a)pyrene Benzo(ghi)perylene Dibenzo(ah)anthracene Indeno(1,2,3-cd)pyrene (Reference: Brion and Pelletier, 2005)	Ultrasonic extraction with dichloromethane for 30 min, then shaken overnight, and again ultrasonication for 30 min. Centrifugation for 10 min at 3000 rpm, rotary evaporation to 3-6 ml, nitrogen evaporation to 0.5 ml. Cleanup with Enviropack_ 18 column (3 ml / 500 mg), elution with 10 ml of 75:25 (v/v) pentane: dichloromethane mixture. Concentration with nitrogen to 0.3 ml, addition of 2 ml hexane and concentration again to 0.5 ml.	RTX5-MS (110 °C for 2 min, 25 °C min <sup>-1</sup> to 310 °C, 5 min, held for 15 min)	-*	-*

Table 3. Analytical methods applied by different researchers for the determination of PAHs in marine sediment samples (continued)

PAHs studied	Sample preparation	Column and temperature program used	Recovery (%)	LOD
Naphthalene 2 methyl naphthalene 1 methyl naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene 2 methyl anthracene 9 methyl anthracene Fluoranthene Pyrene 1 methyl pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Perylene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(ghi)perylene (Reference: Culotta <i>et al.</i> , 2006)	Centrifugation for 10 min, addition of Na <sub>2</sub> SO <sub>4</sub> and activated copper.  A. Soxhlet extraction for 24 h, using dichloromethane-pentane 1:1 solvent mixture. Filtration of the extracts through a pre-cleaned Pasteur pipette filled with solvent-rinsed glass wool and pre-cleaned anhydrous Na <sub>2</sub> SO <sub>4</sub> , (previously rinsed with dichloromethane) and concentration in a rotary evaporator to final volume around 2 ml. Evaporation with nitrogen to dryness and dissolution in 1 ml solution containing the perdeuterated internal standards in cyclohexane (0.2 mg l <sup>-1</sup> each): acenaphthene d <sub>10</sub> ; phenanthrene d <sub>10</sub> , chrysene d <sub>12</sub> and perylene d <sub>12</sub> . B. Ultrasonication with pentane-dichloromethane 1:1 v/v C. Ultrasonication with dichloromethane	Equity-5 (40°C for 2 min, 40°C min <sup>-1</sup> to 100°C, 10°C min <sup>-1</sup> to 200°C, 30°C min <sup>-1</sup> to 325°C, held for 8 min)	A. 79-97 B. 35-65 C. 37-81	0.2 µg kg <sup>-1</sup>
Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene, Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene (Reference: Koch <i>et al.</i> , 2005)	Soxhlet extraction for 20 h with dichloromethane, concentration using a rotary evaporator and treatment with activated copper granules to remove sulfur. Concentration to 2 ml and passing through 10 g of activated Florisil packed in a glass column for fractionation. Elution with 20% dichloromethane in hexane	GC-MS -*	90-105	10 ng g <sup>-1</sup>

Table 3. Analytical methods applied by different researchers for the determination of PAHs in marine sediment samples (continued)

PAHs studied	Sample preparation	Column and temperature program used	Recovery (%)	LOD
Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a)anthracene Triphenylene Chrysene Benzo(b)fluoranthene Benzo(j)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene (Reference: Filipkowska <i>et al.</i> , 2005)	For GC analysis: Centrifugation, extraction with acetonitrile by ultrasonication (15 min) and centrifugation again (2500 rpm, 10 min). Reextraction of acetonitrile fractions in the system: acetonitrile extract:water:benzene 10:10:1 (v/v/v). Evaporation of the benzene extract to dryness in a rotavapor. Dissolution of the residue in 4ml of acetonitrile and cleanup by TLC. Dissolution again in acetonitrile (0.5 ml) and cleanup on a column with copper to remove sulphur. Final elution with acetonitrile. For HPLC analysis: The same procedure, without use of copper.	GC-MS: Varian, CP-Sil 8 CB Low Bleed/MS and VF-5 MS (120 °C for 2 min, 30 °C min <sup>-1</sup> to 240 °C, held for 4 min, 25 °C min <sup>-1</sup> to 275°C, held for 19 min, 5 °C min <sup>-1</sup> to 280 °C, held for 11 min)  HPLC-DAD: Merck Superspher 100 RP-18 column with Merck Lichrospher 100 RP-18 end-capped precolumn Mobile phase acetonitrile:water 95:5 (v/v), at a flow rate 0.4 ml min <sup>-1</sup> , at room temperature. Spectrum scan 220–360 nm (PAHs determined at 254 nm).	GC-MS: 53 – 73, except phenanthrene (47) and anthracene (21)  HPLC-DAD: 64-92	GC-MS: 0.05-0.30 µg ml <sup>-1</sup>  HPLC-DAD: 0.10-0.70 µg ml <sup>-1</sup>
Naphthalene Phenanthrene Anthracene Fluoranthene Pyrene Benz[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene Indeno[1,2,3-cd]pyrene (Reference: Librando <i>et al.</i> , 2004)	Soxhlet extraction: with a solution (1:1) n-hexane (99%)/acetone (99.8%)  Supercritical fluid extraction: with co-solvents: n-hexane, methanol and toluene. extractions with supercritical CO <sub>2</sub> performed at temperatures 50 and 80 °C, pressure from 230 to 600 bars. The organic compounds, recovered are dissolved in n-hexane, acetone or their 1:1 solution.	DB-5MS (-*)	Soxhlet extraction: 73.8-89.1  Supercritical fluid extraction: >90, except fluoranthene (88)	*

\* not reported

Table 3. Analytical methods applied by different researchers for the determination of PAHs in marine sediment samples (continued)

PAHs studied	Sample preparation	Column and temperature program used	Recovery (%)	LOD
Benzo[b]thiophene Dibenzothiophene Fluoranthene Benzo[b]naphtho- [2,3-d]thiophene Benzo-[b]naphtho[2,1-d]thiophene Benzo[b]fluoranthene Benzo[k] fluoranthene Benzo-[a]pyrene Benzo[ghi]perylene Indeno[1,2,3-cd]pyrene	Addition of dichloromethane to the sample, shaking and kept for 30 min. Separation of the supernatant and evaporation to dryness in a rotary evaporator. Redissolution of the residue in 0.5 ml of acetonitrile and filtration through a 0.2 µm nylon syringe filter.	HPLC-DAD Column Kromasil 100 C18 Column temperature 30 °C and mobile phase of ultra pure water and acetonitrile, flow 1 ml min <sup>-1</sup> . <u>Conditions 1:</u> Gradient 20% acetonitrile, increased linearly to 100% in 80 min, kept for 20 min and returned to initial conditions in 5 min. Analytes were detected at 290 nm. <u>Conditions 2:</u> Gradient 40% acetonitrile, linearly increased to 100% in 30 min, kept for 10 min and returned to initial conditions in 3 min. Spectra recorded every 0.4 s between 220 and 300 nm every 0.4 nm.	-* Relative errors < 20%, except indeno[1,2,3-cd]pyrene 30%	-*
(Reference: Gimeno <i>et al.</i> , 2003) * not reported				
Naphthalene, Acenaphthylene Acenaphthene, Fluorene Phenanthrene, Anthracene Fluoranthene, Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene	Microwave extraction followed by solid phase microextraction (Two different fibers were used: polydimethylsiloxane and polyacrylate)	WCOT CP-SIL-8 CB (40 °C for 2 min, 10 °C min <sup>-1</sup> to 280 °C, held for 25 min)	58.6-112	0.28-7.66 ng ml <sup>-1</sup>
(Reference: Pino <i>et al.</i> , 2003)				

Table 3. Analytical methods applied by different researchers for the determination of PAHs in marine sediment samples (continued)

PAHs studied	Sample preparation	Column and temperature program used	Recovery (%)	LOD
Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene (Reference: Banjoo and Nelson, 2005)	Ultrasonication at room temperature, filtration through a glass wool pipette, rotary evaporation to 1 ml. Cleanup by miniaturized silica gel chromatographic column with use of activated copper for sulfur removal.	HP 5% phenylmethyl siloxane (90 °C for 1 min, 9 °C min <sup>-1</sup> to 150 °C, for 2 min, 6 °C min <sup>-1</sup> to 220 °C, 7 °C min <sup>-1</sup> to 260 °C, 2.5 °C min <sup>-1</sup> to 280 °C, 6 °C min <sup>-1</sup> to 300 °C, held for 10 min)	75.5-119.1	1 µg kg <sup>-1</sup>
Fluoranthene, Pyrene Benzo(a)anthracene Chrysene Benzofluoranthene Benzo(e)pyrene Indeno[1,2,3-cd]pyrene Benzo[ghi]perylene (Reference: Wu <i>et al.</i> , 2003)	Soxhlet extraction with Dichloromethane/methanol (v/v: 2:1) for 48 h. Cleanup with silica/alumina column chromatography.	HP-5 (50 °C for 1 min, 10 °C min <sup>-1</sup> to 180 °C, for 7 min, 10 °C min <sup>-1</sup> to 230 °C, for 25 min, 20 °C min <sup>-1</sup> to 280 °C, for 5 min)	-*	-*
Anthracene Fluoranthene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene Indeno[1,2,3-cd]pyrene Benzo[ghi]perylene (Reference: Kostopoulou <i>et al.</i> , 2007)	Ultrasonication at room temperature for 15 min, centrifugation for 10 min at 2500 rpm, desulfurization with activated copper, cleanup with silica micro-columns, concentration to 0.5 ml with nitrogen.	HP-MS (80 °C for 1 min, 15 °C min <sup>-1</sup> to 220 °C, held for 1 min, 5 °C min <sup>-1</sup> to 290 °C, held for 15 min)	65-100	1 ng g <sup>-1</sup>

\* not reported



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