

New approach to the assessment of polycyclic aromatic hydrocarbon monitoring data

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are one of the most ubiquitous groups of pollutant, distributed globally in modern marine environments. A number of PAHs are known carcinogens, are bioactive in marine biota, and may be the precursors to carcinogenic daughter compounds. Long-term PAH data from the French Monitoring Program (Mussel Watch), including remote areas of overseas territories, a three year study after the T/V Erika oil-spill, and surface and sediment core data were used to examine PAH source identification and apportionment. The basis for this examination included: an exploratory analysis of multiple regressions, chemical fingerprints using source-specific diagnostic ratios, PAH class identification and the semi-quantitative determination of their regional present-day source profiles in The English Channel, The Biscay Bay and Western Mediterranean regions. A comparison to reference materials such as known hydrocarbon sources and/or contamination from proximal PAH recognized hot-spots was also made. Finally, quantitative multiple source apportionment of PAHs was determined by using different statistical receptor models and multivariate analysis. This approach to marine chemical PAH data, shows that understanding the contributions of the various sources is not only critical for appropriate managing and remediation strategies in coastal areas, it also helps in recognizing spatial and temporal trends of PAH signatures and concentrations, including a comparison to historical information compiled for a given region as well as in determining the toxic profiles of these contaminants in the marine environment. Determining background concentrations of PAHs is also critical in the assessment of marine monitoring data.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widespread organic pollutants, in modern marine and terrestrial environments. A number of PAHs are known carcinogens, are bioactive in marine biota, and may be the precursors to carcinogenic daughter compounds. In contemporary marine environments anthropogenic derived PAHs predominate. In urban and coastal environments multiple sources of PAH usually coexist. Understanding the contributions of the various emission sources is critical to appropriately managing PAH impacts and remediation strategies in coastal areas. A significant current influx of anthropogenic PAHs is entering marine ecosystems, mainly due to the abundant and long-lasting use and exploitation of fossil fuels (carbon and petroleum) as well as the intensity of diverse combustion processes during past industrialization periods and in contemporary developments. The pathways of combustion derived PAHs are mainly: the atmospheric fallout of soot particles (for example from biomass/biofuels, coal, petroleum and diverse waste burning) and watershed runoff, including urban stormwaters, direct coastal big city discharges and surface runoff from roadways. Whereas the pathways of petroleum derived PAHs are mainly from maritime activity spillage (including, for instance, transport and harbor operations...) and accidental oil spills. Naturally occurring PAHs derived mainly from natural fires, natural oil-seeps, eroded bedrock-derived kerogen and coal and early diagenetic processes. However, the concentrations of naturally occurring background PAHs are generally very low and may be determined in dated well stratified and preserved sediment cores. Pre-industrial natural background concentrations in biota may not be determined now, because even the most remote areas are contaminated by the long-range transport of anthropogenic PAHs.

The qualitative and quantitative methods of source apportionment of PAHs are well recognized and it include the exploratory analysis of chemical fingerprints, using source-specific diagnostic ratios, as well as more quantitative source apportionment based on multivariate analysis methods and receptor environment models (Larsen and Baker 2003, Li et al. 2003). The latter authors quantitatively resolve PAH contributions in the urban atmosphere from diverse sources (for instance coal, oil and wood combustion) (Larsen and Baker 2003). More recently few studies show that PAHs may also serve as good tracers of combustion and fossil carbon in various contemporary environments (McCare et al. 2000, Reddy et al. 2002, Mandalakis et al. 2004, White et al. 2005, Mandalakis et al. 2005, Kumata et al. 2006.). The determination of PAHs may thus contribute to more fundamental assessments of fossil carbon contributions in various pools of marine organic matter and organic carbon budgets, carried out in the context of global climate change studies (White et al. 2005, Dickens et al.2004).

The source apportionment methods of PAHs rely on the analysis of chemical profiles/signatures, which are expected to vary with the compound's source, mainly because of different kinetics in the formation of PAH under different conditions. Hence, the "pure" PAH source end-member signatures and PAH isomer ratios are characteristic of the source and may be well identified. However, in the environment and in biota many factors may affect PAH source signatures. These include for instance, compound partitioning, photochemical or metabolic degradation and even transport and deposition dynamics. Therefore, research and monitoring efforts should attempt to include key PAH source markers that will improve the ability to identify the outputs from the source apportionment models. The source receptor models should also be further developed, validated on the coherent databases and rendered more and more user-friendly.

In this presentation we have used PAH data from a French Monitoring Program (RNO Mussel Watch 2001-2007, English Channel, Biscay Bay and Mediterranean French Coast), including recent data from remote areas of overseas territories, a three year post-spill study after the T/V Erika catastrophe in the Biscay Bay, surface sediment and selected data from dated sediment cores. The analysis of the Rhône delta sediments included different suites of PAHs such as unsubstituted parent compounds, alkyl-substituted homologues (C-PAH) and unsubstituted sulfur heterocycle and their alkyl-substituted compounds (SPA and C-SPA). The concentrations were determined for more than 40 individual compounds and also groups of their alkyl-substituted homologues. PAH source identification and apportionment included: the exploratory analysis of multiple regressions, chemical fingerprints and PAH regional present-day source composition and profiles in The English Channel, Biscay Bay and Western Mediterranean regions.

Sampling, analysis and source apportionment calculations

The sampling sites (about 80) were located in the English Channel, the Atlantic Ocean and the Mediterranean Sea. Each sample consisted of a pool of 20 mussels of approximately the same size. The mussels (*Mytilus edulis* or *Mytilus galloprovincialis*) and Pacific oyster (*Crassostrea gigas*) were collected each year between 2001 and 2007 during the same period, i.e., in late November or early December. This avoided possible differences of contaminant concentrations due to seasonal variations related to the spawning period and/or physiological states of the molluscs. The protocol used for sample collection handling and processing is in accordance with JAMP/ OSPAR guidelines for the monitoring of contaminants in biota and includes the depuration of living mussels before they are shucked, homogenized and stored at -20°C before freeze-drying (OSPAR, 2000). After freeze-drying the samples were stored in the dark at room temperature until further analysis.

About 5 grams of dry weight samples were extracted with dichloromethane using an automated pressurized solvent technique. The lipids were removed from the extracts by Gel Permeation Chromatography (BIO-Beads SX-3 200-400 Mesh, 460 mm x 26 mm column). The clean-up and fractionation of all organic extracts of mollusc samples were made by adsorption chromatography on the silica gel (on top) and alumina (on bottom) columns, with both sorbents deactivated with 5% water (by weight). The first two fractions eluted with hexane and hexane/DCM were separately analysed for PAHs.

The instrumental analysis of PAHs in mussels and sediments was performed by high-resolution gas chromatography fitted with a mass selective detector (MSD; Agilent 6890/5973). Internal QA/QC procedures including laboratory and field blanks, analyses of replicate samples for precision determination (below +/- 5 % for individual compounds), the use of internal recovery perdeuterated standards (phenanthrene-d₁₀, perylene-d₁₂ or benzo[e]pyrene-d₁₂) added to each sample before extraction (higher than 70%). Analyses of Standard Reference Materials (SRM 1491, SRM 2977 from the National Institute of Standards and Technology NIST and EC-2 from The National Water Research Institute – NWRI) are routinely incorporated into each batch of samples and used to monitor the overall accuracy of the method. The laboratory proficiency for PAH analysis is also evaluated through participation in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) intercomparison exercises (obtaining satisfactory and better z scores). The analysis of the shellfish samples included different suites of PAHs such as unsubstituted parent compounds and their alkyl-substituted homologues. The concentrations were determined for more than 40 individual compounds and also for a group of summed alkyl-substituted homologues (Table 1).

Table 1: List of parent and alkyl substituted PAHs and sulfur heterocyclic PAHs determined, abbreviations, molecular weights, and internal standards used as references for quantitation.

Compound name	Abbreviation	Molecular Weight	Internal standard
PAHs and alkyl substituted homologues			
Naphthalene	Naphtalene	128	Acenaphthene-d ₁₀
C1-naphthalenes	C1-N	142	Acenaphthene-d ₁₀
C2-naphthalenes	C2-N	156	Acenaphthene-d ₁₀
C3-naphthalenes	C3-N	170	Acenaphthene-d ₁₀
C4-naphthalenes	C4-N	184	Acenaphthene-d ₁₀
Acenaphthylene	Acenaphthylene	152	Acenaphthene-d ₁₀
Acenaphthene	Acenaphthene	154	Acenaphthene-d ₁₀
Fluorene	Fluorene	166	Fluorene-d ₁₀
C1-fluorenes	C1-F	180	Fluorene-d ₁₀
C2-fluorenes	C2-F	194	Fluorene-d ₁₀
Phenanthrene	Phenanthrene	178	Fluorene-d ₁₀
C1-phenanthrenes/anthracenes	C1-P	192	Fluorene-d ₁₀
C2-phenanthrenes/anthracenes	C2-P	206	Fluorene-d ₁₀
C3-phenanthrenes/anthracenes	C3-P	220	Fluorene-d ₁₀
Anthracene	Anthracene	178	Fluorene-d ₁₀
Fluoranthene	Fluoranthene	202	Pyrene-d ₁₀
Pyrene	Pyrene	202	Pyrene-d ₁₀
Retene	Retene	232	Pyrene-d ₁₀
C1-pyrenes/fluoranthenes	C1-PY	216	Pyrene-d ₁₀
C2-pyrenes/fluoranthenes	C2-PY	230	Pyrene-d ₁₀
Benz[<i>a</i>]anthracene	B[<i>a</i>]anthr	228	Benz[<i>a</i>]anthracene-d ₁₂
Triphenylene	Triphen	228	Benz[<i>a</i>]anthracene-d ₁₂
Chrysene	CHR	228	Benz[<i>a</i>]anthracene-d ₁₂
C1-chrysene	C1-CHR	242	Benz[<i>a</i>]anthracene-d ₁₂
C2-chrysene	C2-CHR	256	Benz[<i>a</i>]anthracene-d ₁₂
Benzo[<i>b</i>]fluoranthene		252	Benz[<i>a</i>]anthracene-d ₁₂
Benzo[<i>k</i>]fluoranthene	BFLs	252	Benz[<i>a</i>]anthracene-d ₁₂
Benzo[<i>j</i>]fluoranthene		252	Benz[<i>a</i>]anthracene-d ₁₂
C1-Benzofluoranthenes	C1-BFLs		Benz[<i>a</i>]anthracene-d ₁₂
Benzo[<i>e</i>]pyrene	B[<i>e</i>]py	252	Benz[<i>a</i>]anthracene-d ₁₂
Benzo[<i>a</i>]pyrene	B[<i>a</i>]py	252	Benz[<i>a</i>]anthracene-d ₁₂
Perylene	Perylene	252	Benz[<i>a</i>]anthracene-d ₁₂
Indeno[1,2,3- <i>cd</i>]pyrene	Indeno-Pyr	276	Benz[<i>a</i>]anthracene-d ₁₂
Dibenz[<i>a,h</i>]anthracene	DBA	278	Benz[<i>a</i>]anthracene-d ₁₂
Benzo[<i>ghi</i>]perylene	B(<i>ghi</i>)perylene	276	Benz[<i>a</i>]anthracene-d ₁₂
Sulfur-heterocyclic compounds and alkyl substituted homologues			
Dibenzothiophene	DBT	184	Fluorene-d ₁₀
C1-dibenzothiophenes	C1-DBT	198	Fluorene-d ₁₀
C2-dibenzothiophenes	C2-DBT	212	Fluorene-d ₁₀
C3-dibenzothiophenes	C3-DBT	226	Fluorene-d ₁₀
Benzonaphthothiophenes	BNTs	234	Pyrene-d ₁₀
C1-benzonaphthothiophenes	C1-BNTs	248	Pyrene-d ₁₀

Two mixture analysis approaches were adopted, using Alternating Least Squares (ALS) and Multivariate Curve Resolution (MCR) calculation techniques. Both methods provide PAH source amounts apportionment in each sample as well as PAH characteristic source profiles. A comparison of these profiles was also made to known hydrocarbon sources and contamination from proximal PAH recognized hot-spots. The MCR source analysis is constrained to only two sources of PAH in the mussel samples i.e.: i) pyrogenic/combustion and ii) petrogenic/petroleum.

PAH concentration levels in molluscs along the French coast

Briefly, the ranges of summed concentrations of parent (Σ PAH) and alkyl homologues (Σ C-PAH) are presented in Figure 1. The median concentrations determined in The English Channel, Biscay Bay and the Western Mediterranean were respectively 110, 138, 85 $\mu\text{g}/\text{kg dw}$ for unsubstituted Σ PAH and 128, 139, 172 $\mu\text{g kg}^{-1} \text{ dw}$ for alkyl substituted homologues Σ C-PAH (N=187, 214, 96 for each coast respectively). The concentration ranges spanned almost over almost 2 orders of magnitude, indicating significant spatial gradients and the presence of very low and very high contamination areas. Most of the sites show a present-day, chronic, intermediary contamination by PAHs of marine intertidal shellfish, located close to the continental loads, yet away from the direct sources of these compounds. The hot-spots are clearly identified by PAH levels and are located near harbours, big coastal urban centres and big French estuaries especially of the Seine river. Only a 5th percentile of all sampling sites presents the low contamination levels of PAH, when evaluated against “low indicator PAH concentrations” proposed by the ICES Marine Chemistry Working Group (ICES 2008). However, natural background concentrations of PAHs would be lower than the proposed “low concentrations” established as the median of the 10th percentile for the different monitoring datasets of PAH in OSPAR regions, including remote/pristine areas i.e. those likely to have relatively low anthropogenic current inputs (ICES 2008).

Furthermore, geographical differences of PAH levels in shellfish along the entire French coast are marked by wider ranges of parent PAH in English Channel and of alkyl homologues in Biscay Bay (Fig. 2.). This may indicate a predominant source of combustion PAHs in The Channel and more oil PAH contamination in the Biscay Bay.

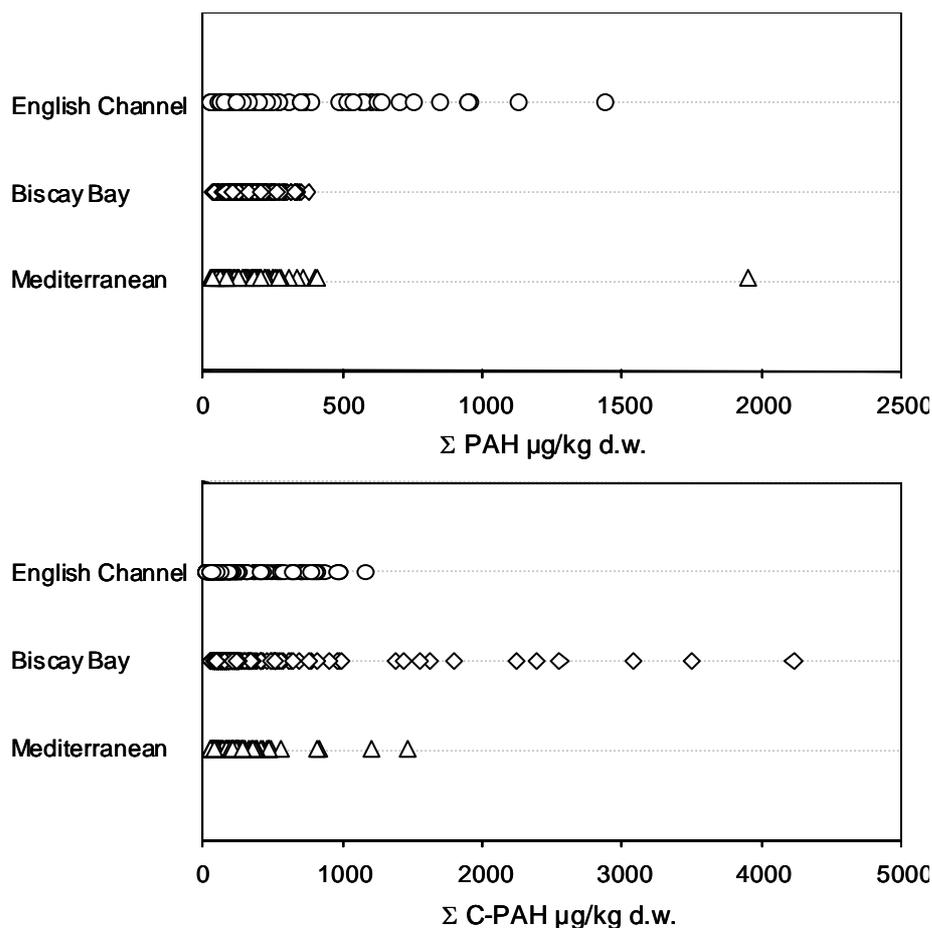


Figure 1. Ranges of summed concentrations of parent (Σ PAH) alkyl PAH (Σ C-PAH) in mollusc samples along three maritime shorelines in France; concentrations are in $\mu\text{g/kg}$ of dry weights.

Diagnostic ratios, chemical patterns and source apportionment of PAHs in molluscs

A wide range of source and weathering biomarkers and indicators were identified within series of PAHs and aliphatic hydrocarbons. Most of these efforts attempt to distinguish between combustion and petrogenic hydrocarbons. Christensen *et al.* (2004) have statistically analysed almost 100 different diagnostic ratios in their efforts to establish an integrated methodology for forensic oil spill identification. However, these methods apply rather to accidental oil spill assessments and less to the chronic non-point PAH monitoring data. Moreover the use of many source ratios requires expert knowledge and very often provides mainly qualitative results.

It appears that summed concentrations of parent versus alkyl PAHs (without low molecular compounds) are a somewhat simple, though fairly sensitive, gauge of combustion and petroleum chronic contamination in intertidal molluscs. However, a practical difficulty is a relative paucity of extended databases for alkyl PAHs from regional monitoring programs. Fairly good correlations between parent and alkyl PAH are shown for the data set of the French Mussel Watch (Figure 2.). The data points split into two distinct classes, which may be roughly divided into the sites with high Σ C-PAH/ Σ PAH ratios ($> 1,5$) and those with low ratios ($< 1,5$). The linear distribution of Σ C-PAH versus Σ PAH concentration values in molluscs implies uniformity of their source material (Fig. 2). It also suggests that the PAH in intertidal shellfish results from a mixing between pyrogenic and combustion suites of PAH. Such discrimination suggests also that the two source models could be applied to apportion PAH between these two sources. Furthermore, consistent geographical separation may be found in both groups having extreme Σ C-PAH/ Σ PAH ratios: sites in the south-west of the Biscay systematically have high ratios and those in the Seine Bay have low ratios. Moreover,

the correlation uses almost all PAHs and their homologues determined in our samples and not a few individual isomers often used as diagnostic PAH ratios (Larsen and Baker 2003).

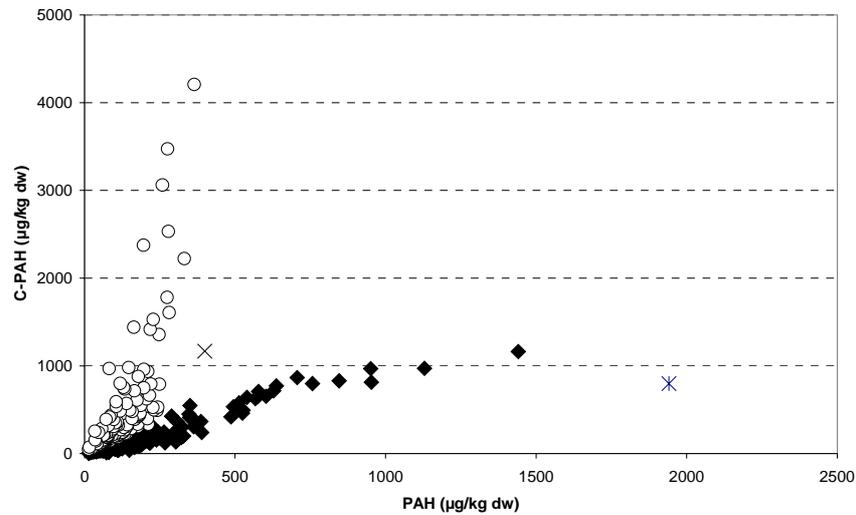


Figure 2. Relationship between unsubstituted Σ PAH and their alkyl substituted homologues Σ C-PAH in shellfish.

The examination of the mean PAH chemical patterns/profiles for the sites with high and low Σ C-PAH/ Σ PAH ratios further enhances source signature identification (Figure 3). The “combustion PAH profile” in shellfish included the following features: (i) a higher proportion of four-, five- and six-ring PAHs (including: fluoranthene, pyrene, chrysene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, indeno[*cd*]pyrene and benzo[*ghi*]perylene) and (ii) a lower relative proportion of alky-homologues. The “oil PAH profile” show: (i) a very high proportion of alkyl-phenanthrenes and alky-dibenzothiophenes; (ii) higher amounts of homologues with increasing substitution alkyl-phenanthrenes and alky-dibenzothiophenes (i.e. a lower proportion of mono- and di-methyl than tri-methyl homologues); (iii) a very low relative amounts of parent PAHs. These fairly even patterns of PAH composition correspond on the one hand to a persistent airborne and river-borne mixture of chemically stable compounds associated with solid particles which may be found in urban atmosphere and marine sediments (Gschwend and Hites 1981), and on the other hand they represent more petroleum-like chronic inputs of hydrocarbons, which may be found in marine harbours, marinas, offshore activities and continuing operational small scale spills. Both patterns overlap and should be further quantitatively apportioned in all mollusc samples.

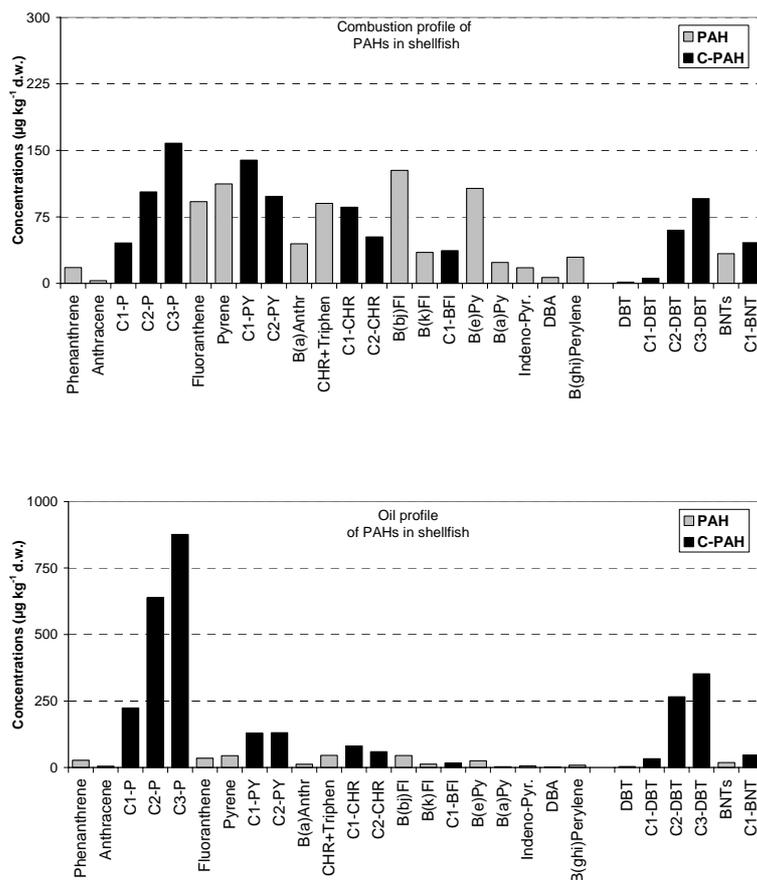


Figure 3. Chemical patterns/profiles of PAHs in intertidal molluscs; mean concentrations from sites with high and low Σ C-PAH/ Σ PAH ratios; compound abbreviations are given in table 1.

The quantitative PAH source apportionment was carried out on all 2001-2007 data from The English Channel, Biscay Bay and the Mediterranean. At the beginning, the analysis was constrained to only two sources of PAH: i) pyrogenic/combustion and ii) petrogenic using the Multivariate Curve Resolution (MCR) calculation technique. However, the Alternating Least Squares (ALS) model may resolve to more sources. In the present example, the results of the three sources for PAH amount apportionment is given. The third source is also attributed also to oil type contamination, and its profile differs only in the relative proportion of di-methyl and tri-methyl phenanthrenes and dibenzothiophenes that are present in higher proportions (Figure 4).

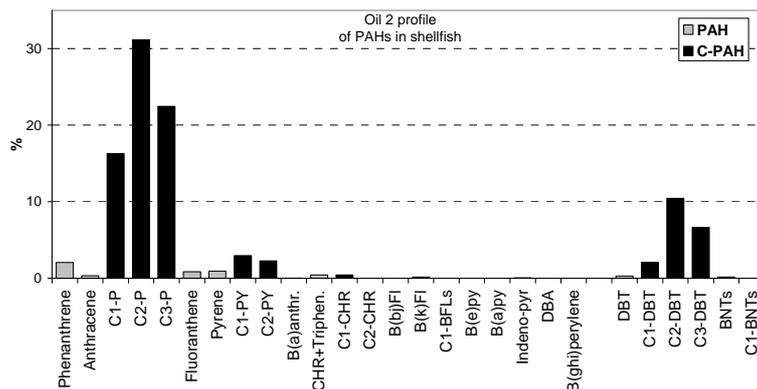


Figure 4. Oil 2 source profile obtained from ALS model (% contribution for each compound and group of compounds).

Finally, the geographical trend of all three source contributions to the total PAH concentrations in shellfish are presented in Figure xx. In areas with the highest contamination by PAH, different sources may be distinguished. In bay of Seine combustion components represent about 70% of PAHs. The remaining 30% of total PAH balance originates from petrogenic hydrocarbons. Similar PAH source apportionment may also be found in the roadstead of Brest. These results suggest that urban combustion PAH inputs may be quite high, and overlap the petrogenic component, notwithstanding intense shipping activities in both areas. However, at another site with high PAH contamination in The English Channel, at the Cherbourg harbour area, the mean petrogenic PAH component is more than 70 % of total. The source profiles for these stations show both types of “oil” contamination. In the Biscay bay the high petroleum like PAH contamination may also be clearly identified in the region of Morbihan (Le Croisic) and in the south-west between the Adour estuary and the Spanish border at Henday-Chingoudy. The Morbihan sites may still bear T/V Erika oil spill traces, especially in the samples collected in 2001. While very high petrogenic PAH contamination in the south-western part of Biscay bay at the French/Spanish border may be related to refinery activities in this area. In the Mediterranean, pollution in the areas with higher PAH contamination may also be assigned to petrogenic sources (for instance at the mouth of the Hérault, in Toulon and at the Golfe de la Napoule). However, further examination of PAH source contributions at sites with medium and low PAH levels indicate that the combustion component predominates more frequently.

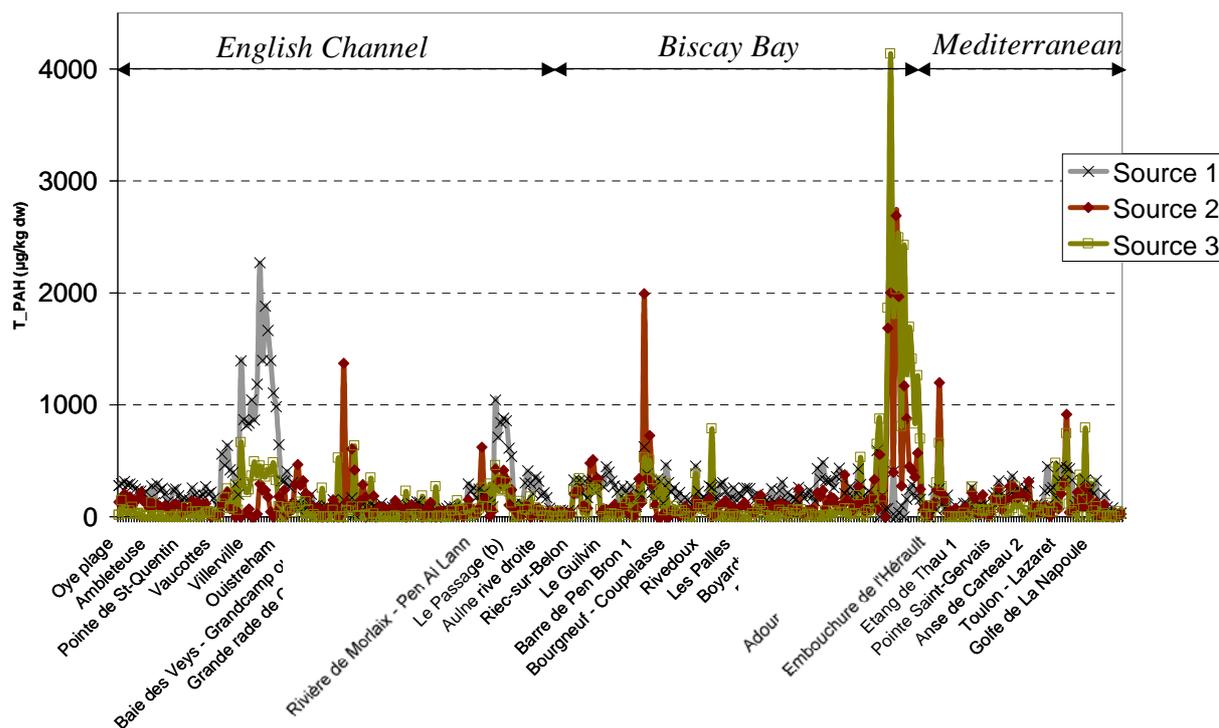


Figure 5. Geographical trend of different source contributions based on alternative least squares calculation (ALS) model to the total PAH concentrations in shellfish. Symbols represent: x combustion; ♦ oil 1 type; □ oil 2 type.

The results of this study provide “pure” source profiles of PAH in the shellfish collected along the intertidal habitats of the French coast. Three profiles were identified and two were assigned to petrogenic contamination and one to combustion source derived PAHs. The quantitative apportionment of PAH sources let us to identify geographical trends in PAH inputs to the various littoral regions in France. Two highly contaminated regions in the bay of the Seine and the Brest roadstead show significant inputs of combustion PAHs. Further study will allow identifying point or not point sources of such PAH inputs to these areas, and will let eventually to guide remediation actions. The petrogenic contamination was strong in different regions along coastline of France. The inputs of petrogenic PAH may be more easily attributed to the specific sources. This study demonstrate also that the analysis of alkyl substituted PAH homologues provide powerful marker compounds in the source apportionment efforts. However, the monitoring programs should also include the analysis of new key PAH indicator compounds that will allow to better quantifying other PAH sources in marine ecosystems, such as biomass combustion and different fossil fuels combustion (coal, oil, diesel, gasoline...). Finally, combining PAH data with other source chemical signatures (for instance Pb stable isotopes, stable carbon isotopes...) will further improve our ability to resolve PAH source profiles and amounts in marine environments.

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