ORIGINAL RESEARCH ARTICLE

Comparison of PCBs and PAHs levels in European coastal waters using mussels from the *Mytilus edulis* complex as biomonitors ☆

Michał Olenycz [a],*, Adam Sokołowski [a], Agnieszka Niewińska [a],
Maciej Wołowicz [a], Jacek Namieśnik [b], Herman Hummel [c], Jeroen Jansen [d]

[a] University of Gdańsk, Institute of Oceanography, Gdynia, Poland
[b] Chemical Faculty, Gdańsk University of Technology, Gdańsk, Poland
[c] Netherlands Institute of Ecology, Centre for Estuarine and Marine Ecology, Yerseke, The Netherlands
[d] IMARES, Den Helder, The Netherlands

Summary   Mussels from the *Mytilus edulis* complex were used as biomonitors for two groups of organic pollutants: polychlorinated biphenyls (PCBs, congeners: 28, 52, 101, 118, 138, 153 and 180) and polycyclic aromatic hydrocarbons (PAHs, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz (a,h)anthracene, benzo(g,h,i)perylene) at 17 sampling sites to assess their relative bioavailabilities in coastal waters around Europe. Because of the temporal differences in PCBs and PAHs concentrations, data were adjusted using Seasonal Variation Coefficients (SVC) before making large-scale spatial comparisons. The highest concentrations of PCBs were found near estuaries of large rivers flowing through urban areas and industrial regions. Elevated bioavailabilities of PAHs

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occurred in the vicinity of large harbors, urban areas, and regions affected by petroleum pollution as well as in some remote locations, which indicated long-range atmospheric deposition.

1. Introduction

The contamination of coastal waters by polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) and their potentially toxic effects on marine organisms has received considerable research focus for many years. Particulate-bound fractions of organic pollutants are introduced into the marine environment mostly with atmospheric deposition and riverine and surface run-off (Porte and Albaiges, 1993). PCBs and PAHs can be transported over vast distances by both the atmosphere and waters; hence, these compounds are often detected in locations that are remote from original sources. Because of their hydrophobic nature, PCBs and PAHs associate rapidly with organic particles suspended in water columns and deposits on sea floors (Ghosh et al., 2003). Suspended and sedimented particulate-bound forms and aqueous phases are the most bioavailable fractions of PCBs and PAHs metabolized by organisms (e.g., filter-feeding bivalves and detritivorous polychaetes) (De Voogt et al., 1989; Lake et al., 1990).

PCBs in the marine environment originate solely from human activity (Sanchez et al., 1993). Before their production and usage had been banned in many countries in the 1970s, mixtures of different PCBs (i.e., Aroclor in Europe and the USA, Sovol in the former USSR) were used extensively for cooling-agent manufacture, for capacitors and transformers, as hydraulic fluids, paint additives, and in manufacturing carbonless copy paper (Boon and Duinker, 1986; Okay et al., 2009; UNEP, 2003). PAHs originate primarily from the incomplete combustion of fossil fuels and biomass (pyrolitic PAHs), slow maturation of organic matter (petrogenic PAHs), and the short-term degradation of organic matter. Although these processes can be natural (e.g., forest fires), most PAHs in the marine environment come from anthropogenic sources (coal-fired heating plants, oil spillages, industrial and urban wastes) (McElroy et al., 1989; Neff, 1979). Each of these processes creates a characteristic chemical pattern that permits identifying the origin of PAHs (Budzinski et al., 1998; Lake et al., 1979; Neff, 1979).

Despite bans of PCBs in many countries being in effect since the 1970s, they are still distributed ubiquitously throughout the environment because of their persistence and slow degradation. Elevated levels of polychlorinated biphenyls are observed primarily in coastal and estuarine marine waters where they can severely impact resident biota, in particular sedentary filter-feeding bivalves and bottom-dwelling polychaetes (Hickey et al., 1995; Lake et al., 1990). Prolonged exposure to PCBs and PAHs can affect many physiological and biochemical processes in living organisms. For example, some of the well-known toxic effects of PCBs are dermal cancerogenity, liver damage, and disruptions in reproduction and ontogenic development (Newsted et al., 1995; Okumura et al., 2004; Safe, 1989; Sapozhnikova

et al., 2004; van den Berg et al., 1998). The principle toxic mechanism of PAHs is narcosis, which alters cell membrane function. PAHs have been identified as possibly carcinogenic and teratogenic in vertebrates (e.g., fish), but not yet in invertebrates (Burgess, 2009; Hawkins et al., 1988). In contrast to PCBs, whose concentrations increase in the food web, those of PAHs decrease. Although the molecular weights and octanol/water partition coefficients (log K_{ow}) of PCBs and PAHs overlap partially, PAHs "biodilute" in the food chain presumably because of their rapid metabolism and limited assimilation at higher trophic levels (Amiard-Triquet and Rainbow, 2011; Takeuchi et al., 2009). The bioaccumulation and biomagnification of toxic and carcinogenic PAHs and PCBs still directly affect local biological products in certain areas, which, in turn, require imposing restrictions on human consumption. Thus, extensive biomonitoring programs have been implemented in many countries to determine the current status of PCBs and PAHs and to predict changes in their environmental levels. Quantifying these organic pollutants in marine biomonitors permits making large-scale geographical comparisons (Goldberg, 1975).

This study was designed to assess contamination levels of PCBs and PAHs in different coastal areas in Europe. Concentrations of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in the soft tissues of sentinel mussels of the *Mytilus* complex have been used as a proxy of the environmental levels of these compounds. The genus is used widely in international monitoring programs (e.g., Mussel Watch in the USA, RNO in France) because of its broad distribution, sedentary life mode, high tolerance to a wide range of environmental conditions, and the ability of accumulating chemicals in their tissues in concentrations proportional to levels in the external environment (Goldberg et al., 1978; Phillips, 1978; Webster et al., 2006). Previous studies have indicated that concentrations of PCBs and PAHs in mussels can vary throughout the year (Boon and Duinker, 1986; Hummel et al., 1990; Piccardo et al., 2001; Webster et al., 2006). Temporal fluctuations in the soft tissue concentrations of organic contaminants are linked directly to the availability of food, hydrological conditions, and internal factors such as physiological condition, age, size, and lipid content (Baumard et al., 1998; Boon and Duinker, 1986; Gilek et al., 1996; Gossiaux et al., 1996; Kuwabara et al., 1986; Widdows et al., 1979).

2. Material and methods

2.1. Sampling and tissue preparation

The mussels were sampled between April 2003 and October 2004 at 17 sampling sites in European coastal waters as follows: the Bay of Faxaflói (Iceland), the Baltic Sea, the North Sea, the English Channel, the Bay of Biscay, the Med-

Table 1   Details of sampling campaigns (site, region, site code, depth and date).

Sampling site	Region	Site code	Depth [m]	Sampling month
Hvassahraun	Faxaflói Bay	HVA	Intertidal	Aug 2004
Reykjavik		REY	Intertidal	Jul 2004
Askö	The Baltic Sea	ASKO	1	Apr 2003
The Gulf of Gdańsk		GDA	38	Oct 2003; Jan, Apr 2004
Mecklenburg	The North Sea	MEK	1	Apr 2003
Grevelingen		GRE	0.5	Jul, Oct 2003; Jan, Apr 2004
Westerschelde		WES	Intertidal	Jul, Oct 2003; Jan, Apr 2004
Somme	The English Channel	SOM	Intertidal	Oct 2004
Seine		SEI	Intertidal	Oct 2004
Le Conquet		CON	Intertidal	Oct 2004
Loire	The Bay of Biscay	LOI	Intertidal	Oct 2004
Ile de Ré		RE	Intertidal	Jul, Aug 2003; Jan 2004
Bidasoa		BID	Intertidal	Apr, Jul 2004
Marseille	The Mediterranean Sea	MAR	6	Apr 2004
Oristano		ORI	6	Apr 2003
Santa Giusta		GIU	6	Apr 2004
Crimea	The Black Sea	CRI	1	Jul 2003

iterranean Sea, the Black Sea (Table 1). In tidal zones, bivalves were collected manually from rocky and sandy bottoms during emersion, while in tideless areas mussels were dredged from research vessels or collected by scuba divers in sublittoral zones at depths of 1—38 m (Table 1). Individuals measuring 20—30 mm shell length found at all the sampling sites were selected for further analysis. This made tissue concentrations comparable, as size sometimes affects concentrations of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in bivalve soft tissues (Gilek et al., 1996; Kuwabara et al., 1986). Immediately after sampling, the live mussels, which were kept wet and cool, and samples of sea water collected from the same site, were transported to the laboratory. The water was filtered through Whatman GF/C filters. The mussels were held in filtered water at temperature and salinity corresponding to those at the sampling site for 24 h to remove gut content (Hofelt and Shea, 1997). The soft tissues were then dissected from 30 to 55 mussels from each site and air-dried individually at 55°C to a constant weight (usually for 48 h) in pre-weighed polythene vials to obtain individual soft tissue dry weight (DW). Dry tissues were subsequently grouped into 4—6 pools of 5—10 individuals each (according to availability) to obtain 1 g. This was homogenized in a standard ceramic mortar. Samples were stored for a short time in PP (polypropylene) vials in the dark at 8°C until analysis.

2.2. Chemicals

The following reagents were used: ABTS [2,2′-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid)]; Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid); Folin—Ciocalteu (all purchased from Sigma-Aldrich). The chemicals used for gas chromatographic analyses were: dichloromethane; methanol; cyclohexane (Merck KgaA); silica gel (40 μm, J.T. Baker, Holland); a mixture of 16 PAHs (each compound concentration of 2000 μg cm^{-3}), (Restek Corporation); a solution

of Naphthalene-d8 in dichloromethane (concentration of 2000 μg cm^{-3}), (Supelco); solution of benzo(a)anthracene in dichloromethane (concentration of 2000 μg cm^{-3}), (Supelco); standard solutions of seven PCBs in isooctane (each compound concentration of each compound 100 μg cm^{-3}), (Restek Corporation).

2.3. Analytical procedures

Samples (1 g) were hydrolyzed in 4 N methanolic KOH solution at boiling temperature for 4 h and then extracted with cyclohexane. These extracts were cleaned in silica gel columns. The volume of eluates was then reduced to 0.3 cm^3 under a nitrogen stream, and 0.002 cm^3 of the extract was injected into a GC—MS system in three repetitions. Analyses were performed using a TraceGC gas chromatograph (Thermoquest) with a TraceMS mass spectrometric detector (Thermoquest) with electron ionization and an on-column injector. The capillary column was as follows: Restek Rtx$^®$ 5-MS, 30 m, 0.25 mm ID, 0.25 μm df. The following temperature program was selected as an optimal for substances with considerably divergent boiling temperatures: 40—120°C (40°C min^{-1}); 120—280°C (5°C min^{-1}); 280°C held for 12 min. The carrier gas was helium maintained at a constant pressure of 70 kPa. All PCBs and PAHs analyzed with their limits of detection (LOD) and quantification (LOQ) are presented in Table 2. Tissue concentrations of PCBs and PAHs are presented as the arithmetic mean of three repetitions and standard deviation.

2.4. Coefficient of seasonal variation

Since concentrations of organic compounds in soft tissues of mussels can vary seasonally (Bodin et al., 2004; Namieśnik et al., 2008), this effect must be accounted for prior to large-scale spatial comparisons. Since the mussels for the current study were collected in different geographical regions, the

Table 2 Limit of quantification and limit of detection of analyzed polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in mussels [ng g^{-1} DW].

Analyte	Analyte abbreviation	Limit of quantification (LOQ)	Limit of detection (LOD)
2,4,4′-Trichlorobiphenyl	PCB 28	1	0.3
2,2′,5,5′-Tetrachlorobiphenyl	PCB 52	1	0.3
2,2′,4,5,5′-Pentachlorobiphenyl	PCB 101	1	0.3
2,3′,4,4′,5-Pentachlorobiphenyl	PCB 118	1	0.3
2,2′,3,4,4′,5′-Hexachlorobiphenyl	PCB 138	1	0.3
2,2′,4,4′,5,5′-Hexachlorobiphenyl	PCB 153	1	0.3
2,2′,3′,4,4′,5,5′-Heptachlorobiphenyl	PCB 180	1	0.3
Naphthalene	Nap	1	0.3
Acenaphthylene	Acy	1	0.3
Acenaphthene	Ace	1	0.3
Fluorene	Fl	1	0.3
Phenanthrene	Phe	2	0.6
Anthracene	An	2	0.6
Fluoranthene	Flu	2	0.6
Pyrene	Py	2	0.6
Benz(a)anthracene	B[a]An	3	1
Chrysene	Chr	3	1
Benzo(b)fluoranthene	B[b]Flu	3	1
Benzo(k)fluoranthene	B[k]Flu	3	1
Benzo(a)pyrene	B[a]Py	3	1
Indeno(1,2,3-cd)pyrene	I[1,2,3-cd]Py	4	1.3
Dibenz(a,h)anthracene	Di[a,h]An	4	1.3
Benzo(g,h,i)perylene	B[g,h,i]Pe	4	1.3

Seasonal Variation Coefficient (SVC; Przytarska et al., 2010) was calculated based on available literature data and the results of this study. The SVC was calculated as the ratio of PCB/PAH concentration at a particular site in a given season and PCB/PAH concentration from the same site in spring. Spring was selected as the reference season as the majority of samples were taken in April (Table 1). Thereby, analyte concentrations in mussels from Askö, the Gulf of Gdańsk, Mecklenburg, Westerschelde, Grevelingen, Bidasoa, Marseille, Oristano, and Santa Giusta Lagoon were included in the analyses without applying the SVC as the samples had been taken in spring. Samples collected in seasons other than spring in Hvassahraun, Reykjavik, Somme, Seine, Le Conquet, Loire, and Ile de Ré were adjusted with SVC before geographical comparison. Given differences in the bioaccumulation patterns of PCBs and PAHs in different biogeographic zones and under divergent environmental conditions, the SVC was computed separately for different European coastal waters according to the climatic features of the individual sites. Data for the Atlantic sites (Hvassahraun, Reykjavik, Somme, Seine, Le Conquet, Loire, and Ile de Ré) were converted accordingly based on the SVC that was calculated for the Westerschelde site, and the data for the Crimea site were adjusted using the SVC for the Marseille site.

2.5. Statistical methods

The homogeneity of variances was tested with Cochran's test and the normality of data with the Kolmogorov−Smirnov test as prerequisites to the parametric approach. Differences in mean concentrations of PCBs and PAHs in mussel soft tissues among seasons and sampling sites were determined separately with one-way ANOVA. The sampling sites were ranked in ascending order of accumulated concentrations and correlation analysis was performed to describe relationships between ranks. Correlation, factor, and PCA (on normalized data) analyses were conducted using STATISTICA 8.1 (StatSoft) with a level of significance $p < 0.05$ (Sokal and Rohlf, 1995). For concentrations below LOD/LOQ the value 0.0 was used for statistical analyses.

3. Results

Since concentrations of PCBs 28, 52 and 180 and PAHs acenaphthene, fluorene, indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene were below LOD at the majority of sites, these compounds were excluded from further analysis.

3.1. Seasonal variability in concentrations of selected PCBs and PAHs

Seasonal variation in concentrations of PCBs and PAHs was determined only for those sites where mussels had been collected in at least three different seasons, i.e. Grevelingen (GRE), Westerschelde (WES), Gulf of Gdańsk (GDA), and Ile de Ré (RE).

Of the seven PCBs examined, the effect of season was apparent only for PCB 101, PCB 138 and PCB 153 (one-way ANOVA, $p < 0.05$), which occurred in mussel tissue in the highest concentrations at WES, GDA and RE. Similar seasonal patterns were observed for all congeners with markedly increased concentrations in spring and summer and lowered values in autumn and winter (Table 3).

Table 3 Concentrations of PCBs in soft tissues of *Mytilus* spp. [ng g^{-1} DW] in different seasons at four sites: Grevelingen (GRE), Westerschelde (WES), the Gulf of Gdańsk (GDA) and Ile de Re (RE) (data are presented as mean and standard deviation, n = 3), (nd — below LOD or LOQ). All values connected by clasp show significant seasonal difference at *$p < 0.05$; **$p < 0.01$; *** $p < 0.001$.

	PCB 101	PCB 118	PCB 138	PCB 153
GRE				
Spring	0.7 ± 0.6	0.3 ± 0.6	1.3 ± 0.6	2.7 ± 0.6
Summer	0.7 ± 0.6	0.7 ± 0.6	1.3 ± 1.5	2.0 ± 1.0
Autumn	nd	nd	0.7 ± 0.6	1.7 ± 0.6
Winter	nd	nd	0.3 ± 0.6	1.0 ± 1.0
WES				
Spring	2.0 ± 1.0	1.3 ± 0.6	8.3 ± 2.1	16.7 ± 6.7
Summer	2.0 ± 1.0	1.7 ± 1.2	11.0 ± 1.7	18.7 ± 3.8
Autumn	0.3 ± 0.6	0.3 ± 0.6	2.3 ± 0.6	4.3 ± 1.5
Winter	0.3 ± 0.6 *	nd	1.3 ± 0.6 ***	3.0 ± 1.0 *
GDA				
Spring	1.3 ± 0.6	1.0 ± 1.0	2.7 ± 1.2	6.7 ± 1.5
Autumn	0.3 ± 0.6	0.3 ± 0.6	0.3 ± 0.6	1.0 ± 0.0
Winter	0.7 ± 0.6	0.7 ± 0.6	1.7 ± 0.6 *	4.7 ± 1.5 *
RE				
Summer	0.7 ± 0.6	0.7 ± 0.6	3.3 ± 1.2	7.0 ± 1.7
Autumn	nd	nd	0.3 ± 0.6	0.7 ± 0.6
Winter	0.3 ± 0.6	0.7 ± 0.6	1.3 ± 0.6 *	2.7 ± 1.5 *

The concentrations of all PAHs, except acenaphthylene, also varied significantly temporally (one-way ANOVA, $p < 0.05$). For the majority of the compounds, elevated soft tissue levels occurred during autumn and winter (Table 4), while the lowest concentrations were generally noted in summer. Incidentally, they were also observed in other seasons at different sites (Table 4). In the southern Baltic Sea (GDA) all PAHs, except phenanthrene and anthracene, were noted at decreased levels in autumn, while the minima for anthracene, fluoranthene, and pyrene were noted in winter and minimal naphthalene was note in autumn on the Atlantic coast of France (RE). The brackish GRE site was the only location where the concentration of naphthalene in mussel tissue was below LOD in winter.

3.2. Spatial variability of concentrations of the analyzed PCBs and PAHs

Concentrations of PCBs and PAHs adjusted with SVC in the soft tissues of the *Mytilus* complex varied significantly among sites (one-way ANOVA, $p < 0.001$ for all compounds).

In order to assess the contamination level of PCBs and PAHs in the coastal waters of Europe, sampling sites were ranked according to the concentrations of organic compounds in mussel tissues (rank 1 corresponds to the highest tissue concentration while rank 17 indicates the lowest tissue concentration). Individual and mean rank values, separately for PCBs and PAHs, were then used to delineate geographical variations of PCBs and PAHs along the European coast. When a concentration of a given PCB or PAH was below LOD, it was assigned

rank 17. The ranks of PCBs and PAHs are presented in Tables 5 and 6, respectively.

Generally, there was consistency in the geographical distribution of different PCBs in various water basins; at sites with elevated levels of a given PCB high tissue concentrations of other congeners were also noted, and at sites where there were low concentrations of a given PCB in mussel tissues were also ranked highly with respect to other congeners (correlation significant for all pair-wise comparisons, $p < 0.022$). High concentrations of all PCBs were noted in mussels on the French coast of the English Channel and the Atlantic coast (SEI, LOI, SOM; mean rank ranged from 1.0 to 2.6), (Table 5). It is noteworthy that the levels of all PCB congeners at the SEI site in the mouth of the Seine River were extreme, and here concentrations of individual congeners exceed at least 2.4-fold the respective concentrations of corresponding congeners at other sites. Elevated concentrations of PCBs were also found in *Mytilus edulis* from the REY site (mean rank 4.6) and in *Mytilus edulis/trossulus* in the western Baltic Sea (MEK, mean rank 5.9) and the Dutch site WES (mean rank 6.0). Intermediate concentrations of almost all PCBs (mean rank between 8.1 and 9.1) occurred in mussels collected in the Bay of Biscay (BID), the southern Baltic Sea (GDA), and the Mediterranean Sea (GIU). However, at the GIU site PCB 118 was noted at a relatively high concentration in mussel tissues (individual rank 6.0). Slightly lowered PCBs levels (mean rank 10.8 and 10.9, respectively) were determined in mussels collected in the Bay of Faxaflói on the western coast of Iceland (HVA) and in the central Baltic Sea (ASKO). Low concentrations of PCBs (mean rank from 12.3 to 13.9) were determined in the Mediterranean Sea (ORI), the brackish inland Lake Grevelingen (GRE), the Black Sea (CRI), and the Bay of Biscay (CON). Exceptions were the CRI and CON sites where increased concentrations of PCB 101 were observed (individual ranks 4.0 and 7.0, respectively). Highly ranked sites included RE on the Atlantic coast of France (mean rank 15.3) and MAR in the Mediterranean Sea (16.8) where the resident mussels showed the lowest concentrations of nearly all PCBs measured.

As in the case of PCBs, ranks of individual PAH concentrations in mussel tissues showed generally similar geographical variation across sites (of 55 pair-wise comparisons R Spearman correlation was significant in 28 cases, all at $p < 0.05$; Table 6). Only ranks assigned to naphthalene and benzo(g,h,i)perylene did not correlate with the respective ranks of any other PAHs. In addition, the overall spatial pattern of tissue levels of individual PAHs corresponded well with the geographical distribution of individual PCBs (of 44 pair-wise comparisons of individual PCB vs. individual PAH, the R Spearman correlation was significant in 34 cases, all at $p < 0.05$); this indicates not too distant sources and similar distribution mechanisms of both groups of organic compounds. Again, no relation was found between naphthalene and benzo(g,h,i)perylene or any of the polychlorinated biphenyls. The highest concentration of the majority of PAHs was noted in the Bay of Faxaflói (REY, mean rank 4.1). In contrast to other PAHs, naphthalene and benzo(g,h,i)perylene were found in very low concentrations (both individual ranks 17.0) at this site. High concentrations of PAHs (mean rank from 5.3 to 6.0) were also noted at the MEK, SEI, CRI, and GDA sites. However, at the SEI and GDA sites, naphthalene occurred in very low concentrations in mussel tissues (individual ranks 17.0 and 13.0 respectively), while at

Table 4 Concentrations of PAHs in soft tissues of *Mytilus* spp. [ng g^{-1} DW] in different seasons at four sites: Grevelingen (GRE), Westerschelde (WES), the Gulf of Gdańsk (GDA) and Ile de Re (RE) (data are presented as mean and standard deviation, n = 3) (nd — below LOD or LOQ). All values connected by clasp show significant seasonal difference at *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$.

	Nap	Phe	An	Flu	Py	B[a]An	Chr	B[b]Flu	B[k]Flu	B[a]Py	B[g,h,i]Pe
GRE											
Spring	41.7 ± 3.5	74.3 ± 4.7	5.7 ± 0.6	16.0 ± 1.7	11.0 ± 1.0	4.3 ± 0.6	6.0 ± 1.0	6.0 ± 1.0	4.3 ± 1.2	2.7 ± 0.6	5.0 ± 1.0
Summer	19.7 ± 3.1	25.3 ± 3.8	4.0 ± 2.0	5.0 ± 2.0	5.0 ± 1.7	1.0 ± 0.0	1.0 ± 1.0	1.0 ± 0.0	0.7 ± 0.6	0.7 ± 0.6	3.0 ± 0.0
Autumn	1227 ± 7.6	176.7 ± 8.5	13.3 ± 2.5	18.3 ± 2.5	12.0 ± 2.6	3.3 ± 1.5	5.7 ± 1.5	6.0 ± 1.0	4.7 ± 1.5	3.7 ± 1.2	4.3 ± 1.5
Winter	nd	128.0 ± 9.8	11.0 ± 2.0	16.0 ± 3.6	11.7 ± 1.5	6.0 ± 1.0	9.7 ± 2.5	14.0 ± 2.6	10.3 ± 2.5	7.3 ± 2.1	12.7 ± 2.5
WES											
Spring	294.3 ± 6.7	57.0 ± 1.7	3.3 ± 1.5	23.3 ± 1.5	13.0 ± 2.0	3.3 ± 1.2	7.7 ± 1.2	10.3 ± 2.1	3.3 ± 0.6	4.0 ± 0.0	3.7 ± 1.5
Summer	nd	104.3 ± 11.2	9.7 ± 1.5	15.0 ± 2.6	10.0 ± 2.6	4.3 ± 1.2	6.7 ± 1.5	9.3 ± 3.2	3.3 ± 1.5	2.7 ± 1.5	nd
Autumn	135.7 ± 3.1	119.0 ± 4.4	16.7 ± 2.1	25.3 ± 2.1	27.0 ± 2.6	8.3 ± 2.1	23.3 ± 1.5	23.3 ± 3.2	17.3 ± 3.2	7.3 ± 1.5	15.7 ± 1.5
Winter	nd	98.7 ± 4.5	19.0 ± 1.7	22.0 ± 2.6	21.7 ± 1.5	5.7 ± 2.1	17.3 ± 2.5	21.0 ± 2.6	15.7 ± 2.3	7.7 ± 1.2	8.7 ± 2.1
GDA											
Spring	10.7 ± 2.1	114.7 ± 7.2	9.3 ± 1.2	18.7 ± 2.1	15.7 ± 2.1	5.3 ± 3.1	7.0 ± 2.6	6.7 ± 1.2	5.0 ± 1.0	6.0 ± 1.0	6.7 ± 1.2
Autumn	9.0 ± 2.0	153.0 ± 6.0	14.7 ± 2.8	13.0 ± 2.6	8.0 ± 1.0	2.3 ± 0.6	3.0 ± 2.0	2.7 ± 0.6	2.0 ± 0.0	1.7 ± 0.6	nd
Winter	177.0 ± 6.6	214.3 ± 9.5	19.3 ± 2.1	34.7 ± 3.5	24.3 ± 2.5	63.3 ± 3.8	18.0 ± 2.6	32.0 ± 3.6	23.7 ± 1.5	9.0 ± 2.6	18.7 ± 2.8
RE											
Summer	52.3 ± 4.9	96.3 ± 4.2	9.3 ± 1.5	11.3 ± 1.5	13.0 ± 1.7	1.7 ± 0.6	3.0 ± 1.0	3.7 ± 0.6	2.7 ± 0.6	1.3 ± 0.6	nd
Autumn	28.3 ± 3.1	133.0 ± 6.2	14.7 ± 1.2	16.0 ± 2.6	13.7 ± 3.1	3.3 ± 1.2	5.3 ± 0.6	5.3 ± 1.5	4.0 ± 1.0	3.3 ± 1.2	2.3 ± 0.6
Winter	94.7 ± 4.2	130.3 ± 5.5	8.7 ± 2.1	9.7 ± 2.1	7.7 ± 3.1	3.0 ± 1.0	3.3 ± 1.5	4.7 ± 1.5	3.3 ± 0.6	2.7 ± 0.6	nd

Table 5 Individual and mean ranks of PCBs concentrations (adjusted with SVC) in soft tissues of *Mytilus* spp. from the European coastal waters.

Site	PCB 101	PCB 118	PCB 138	PCB 153	Mean rank
SEI	1	1	1	1	1.0
LOI	3	3	2	2	2.4
SOM	3	2	3	3	2.6
REY	5	4	6	4	4.6
MEK	9	6	4	5	5.9
WES	7	6	6	6	6.0
BID	9	9	8	7	8.1
GDA	11	9	9	8	9.1
GIU	11	6	12	9	9.3
HVA	14	12	7	10	10.8
ASKO	12	9	12	11	10.9
ORI	14	11	10	14	12.3
GRE	14	13	13	12	13.0
CRI	4	17	17	16	13.5
CON	7	17	17	15	13.9
RE	17	17	14	13	15.3
MAR	16	17	17	17	16.8

Table 6 Individual and mean ranks of PAHs concentrations (adjusted with SVC) in soft tissues of *Mytilus* spp. from the European coastal waters.

Site	Nap	Phe	An	Flu	Py	B[a]An	Chr	B[b]Flu	B[k]Flu	B[a]Py	B[g,h,i]Pe	mean rank
REY	17	1	1	1	1	1	1	1	1	3	17	4.1
MEK	8	7	3	7	5	4	3	6	4	9	4	5.3
SEI	17	4	10	3	4	3	5	2	5	4	2	5.4
CRI	5	2	6	9	3	2	2	9	7	1	17	5.7
GDA	13	3	3	8	6	6	7	7	6	6	1	6.0
ASKO	9	9	4	12	12	5	4	5	3	11	6	7.2
WES	3	15	11	7	7	9	6	4	9	7	5	7.5
GRE	10	10	7	10	9	8	8	8	8	11	3	8.3
HVA	17	11	12	2	2	17	16	4	3	5	17	9.5
BID	4	7	9	15	15	7	9	10	10	16	7	9.8
ORI	6	5	8	15	11	12	10	15	11	14	9	10.5
MAR	12	8	5	17	13	15	12	16	12	2	9	11.0
SOM	2	16	15	5	8	14	11	13	15	13	10	11.0
CON	11	12	16	5	10	11	14	12	14	13	17	12.1
LOI	1	17	17	13	17	13	14	11	13	8	12	12.3
RE	7	14	13	11	16	16	15	14	16	15	12	13.5
GIU	17	13	14	16	15	10	17	17	17	17	17	15.4

the CRI site, the benzo(g,h,i)pyrelene level was ranked highly (individual rank 17.0). Accumulated concentrations of PAHs at the two Dutch sites, WES and GRE, as well as in the central Baltic Sea (ASKO) were lower with mean ranks ranging from 7.2 to 8.3. Intermediate concentrations of PAHs (mean ranks from 9.5 to 11.0) were noted at the HVA site in the Bay of Faxaflói, in the Bay of Biscay (BID), at the ORI site in the Bay of Oristano, the Mediterranean Sea (MAR) and in the English Channel (SOM). At the Icelandic HVA site, the soft tissue concentrations of fluoranthene, pyrene, benzo(b)fluoranthene, and benzo(k)fluoranthene were relatively high (individual ranks: 2.0 for fluoranthene and pyrene, 3.0 for benzo(k)fluoranthene) and 4.0 for benzo(b)fluoranthene. The levels of naphthalene at SOM and benzo(a)pyrene at the MAR site were also elevated

(both individual rank 2.0). Lower concentrations of PAHs in *Mytilus* spp. were found in the Bay of Biscay (CON, LOI, mean ranks 12.1 and 12.3, respectively), and only naphthalene concentration was considerably increased at the LOI site (individual rank 1.0). The sites of the lowest pollution levels with PAHs included RE in the Bay of Biscay and GIU in the Mediterranean Sea (mean ranks 13.5 and 15.4, respectively).

3.3. Factor and PCA analysis on sites and origin of PAHs

In order to determine which organic compounds control the grouping of the sites described by object scores, a plot for

loadings (PCBs and PAHs) is presented in Fig. 1. In the PCA analysis, sites with the highest summary environmental bioavailabilities of PCBs (SEI), Nap (REY) and the other PAHs (LOI and SOM), form outlying groups which can be distinguished from other European sites (Fig. 1). In the factor loading, the first factor accounting for 43.1% of the total variance is marked by the positive loading of the majority of PAH chemicals and the negative loading of naphthalene. The second factor, which is responsible for 28.3% of the total variance, is marked by positive loading of all PCB chemicals. The position of the SEI site confirms the previous finding that PCBs were detected in exceptionally high concentrations in mussels collected in the estuary of the Seine River. The REY site is characterized by a marked loading of PAHs, which supports

the hypothesis that Reykjavik harbor can be considered seriously contaminated with polycyclic aromatic hydrocarbons. The two sites on the French coast, i.e. LOI and SOM, make a separate clustering because of the raised levels of accumulated naphthalene, presumably as an effect of large riverine discharge of this compound to the coastal zone. The Black Sea site CRI was also well isolated from other sites as is reflected in the extreme levels of benzo(a)pyrene in mussels. The resident bivalves are likely exposed to large inputs of organic compounds from combustion processes and the local Russian military harbor of Sevastopol.

Commonly used phenanthrene/anthracene and fluoranthene/pyrene molecular ratios were calculated to determine pyrolitic (Phe/An <10 and Flu/Py >1) or petrogenic
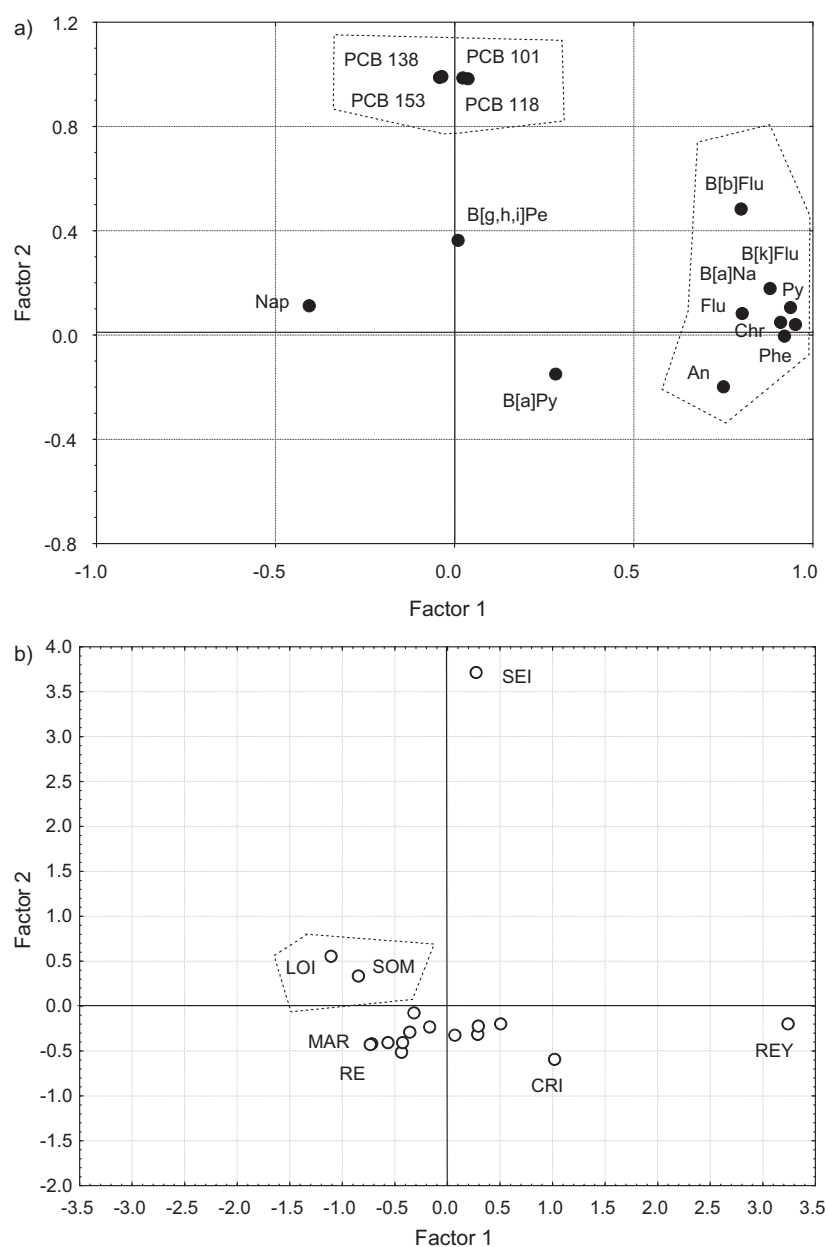

Figure 1 Scatter plots of two-dimensional factor loading (a) and factor scores of individual data in the space (F1 · F2) (b). For abbreviations of sampling sites, PCBs and PAHs see Tables 1 and 2, respectively. The first two factors in the PCA analysis with eigenvalues >1.0 account for 71.5% of the total variance.

(Phe/An >15 and Flu/Py <1) sources of contamination (Baumard et al., 1998). At most sites, PAHs originated from a combination of both pyrolitic and petrogenic processes with the exceptions of the CRI, REY, and MAR sites, where petrogenic PAHs dominated, and the GDA, GRE, MEK and ASKO sites where pyrolitic origin was detected (Fig. 3).

4. Discussion

4.1. Seasonal variability in concentrations of selected PCBs and PAHs

Bioaccumulation of hydrophobic organic compounds, like PCBs and PAHs, in sedentary marine organisms is strongly dependent on their soft tissue lipids (Bright et al., 1995; Livingstone, 1992). Lipid content in bivalves varies with physiological condition and reproduction cycle, increasing markedly during gamete maturation in late winter and early spring, and decreasing during and after spawning in late spring and summer (Gabbott, 1983; Zandee et al., 1980). In addition, lipid content in mussels can be affected by the nutritional condition of the ambient environment. In autumn and winter months when there is a deficiency of food, the utilization of lipid reserves increases to avoid starvation (Gabbott and Bayne, 1973; Hummel, 1985; Widdows et al., 1979). Two mechanisms can be suggested to explain the observed seasonal variations in concentrations of PCB 138 and PCB 153. Firstly, the highly chlorinated structure means the solubility of these compounds is good in lipids, the content of which changes significantly in bivalve tissues throughout the year. Secondly, they are common in marine environments because of the long-term use of them in many European countries in the chemical mixtures Aroclor 1254 and 1260 (Cleghorn et al., 1990; Ivanov and Sandell, 1992). In this study, soft tissue concentrations of PCB 138 and PCB 153 increased in spring and summer (during the pre-spawning period with high food availability) and decreased in autumn and winter (spawning period and limited food abundance). Lee et al. (1996) observed similar patterns in temporal changes in mussels from the southwestern Baltic Sea. The authors suggest that higher concentrations of PCBs in spring and summer can also result from increased water turbidity in the river mouths and estuaries that are major transport routes of PCBs to the coastal zone.

A fairly inverse pattern was observed for PAHs whose concentrations in autumn and winter were higher than in spring and summer (the exception was at RE where the highest PAH concentration was noted in summer). This general temporal cycle is consistent with data from other temperate climate regions such as the Ligurian Coast (Italy) and the west coast of Scotland (Piccardo et al., 2001; Webster et al., 2006). Polycyclic aromatic hydrocarbons and polychlorinated biphenyls are hydrophobic compounds and both occur mainly in tissues with high lipid content (Livingstone, 1992). It is therefore surprising that PAH concentrations increased during autumn and early winter when the lipid content in mussels is relatively low (Prato et al., 2010). One explanation can be the origin of PAHs that includes mainly atmospheric deposition and river run-off. During the heating season in autumn and winter, pyrolitic PAHs are released in substantial amounts into the atmosphere as smoke from burning coal and wood in domestic heating systems or from heating plants (Baumard et al., 1999; Kautenburger and Muller, 1996; Simkova et al., 1996). For example, >5-time increase in PAH levels in winter was noted in the USA and Germany relative to summer because of organic combustion in cold months (Greenberg et al., 1985; Katz and Chan, 1980; Yang and Baumann, 1995). What is more, in winter months a marked increase (4—10 fold) of PAH emissions from motor vehicles is noted in colder periods (Bjorseth and Ramdahl, 1985). Subsequently, elevated concentrations of PAHs in suspended particulate-bound forms are observed in coastal waters near large industrial centers and urban agglomerations resulting in the more intense accumulation of these compounds in filter-feeding organisms like mussels.

4.2. Spatial variability of concentrations of analyzed PCBs and PAHs

4.2.1. Polychlorinated biphenyls

Significant spatial differences were observed between PCBs 101, 118, 138, and 153 concentrations at all 17 sites (Table 7). PCB 153 and PCB 138 occurred at the highest concentrations in soft tissues of *Mytilus* spp. at most sites, while PCB 101 concentration was the highest at the CON and CRI sites (Table 7). Hexachlorinated congeners 138 and 153 were previously reported to predominate in the benthic biota of coastal areas of the western Mediterranean Sea (Porte and Albaiges, 1993) and the Adriatic Sea (Bayarri et al., 2001; Piersanti et al., 2006).

Generally high concentrations of PCBs in mussel soft tissue were found at sites located in the estuaries of large rivers that flow through highly urbanized and industrial areas (Fig. 2, Table 7). Elevated levels of PCBs were also observed in the vicinity of industrial and urban centers. Previous studies show that the main sources of PCB chemicals in marine basins are atmospheric deposition and riverine outflow (Duinker and Bouchertall, 1989; Tolosa et al., 1997). Atmospheric deposition is a dominating factor particularly in open waters, while in coastal areas riverine discharge and surface runoff can make important contributions (Agrell et al., 2001; Fu and Wu, 2006). Although PCBs have not been produced since 1993 when Russia definitively ceased manufacture (AMAP, 2000), sediments are long-term reservoirs that serve as secondary sources of these compounds in coastal systems (Barra et al., 2006).

The highest levels of PCBs both with regard to the sum of all congeners and individual compounds were recorded at the SEI (sum of all PCBs 1120.3 ng g^{-1} DW, mean rank 1.0) and SOM (207.5 ng g^{-1} DW; mean rank 2.6) sites on the French coast of the English Channel, and at the LOI site (301.5 ng g^{-1} DW, mean rank 2.4) in the coastal area of the Bay of Biscay (Fig. 2, Table 7). These sites are located near estuaries of three large rivers, the Seine, the Somme, and the Loire, respectively, that flow through the highly urbanized and intensely industrialized areas of central and northern France. The Seine has been designated the most polluted river in France in large-scale biomonitoring programs of the French coast (Abarnou et al., 1987; Marchand et al., 1989) and even on the scale of the European continent (Duinker and Hillebrand, 1979; Thomas et al., 1984; Pavoni et al., 1987).

Table 7 Concentrations of PCBs (adjusted with SVC) in soft tissues of *Mytilus* spp. [ng g^{-1} DW] from the European coastal waters (nd — below LOD or LOQ). For PCBs abbreviations see Table 2.

Site	PCB 101	PCB 118	PCB 138	PCB 153	Σ
SEI	242.0 ± 15.1	94.7 ± 8.3	279.8 ± 12.5	503.9 ± 13.9	1120.3
LOI	26.0 ± 9.2	9.3 ± 2.3	89.3 ± 6.2	176.9 ± 10.2	301.5
SOM	26.0 ± 9.2	18.7 ± 6.1	50.0 ± 9.4	112.8 ± 9.7	207.5
REY	4.7 ± 0.6	2.9 ± 0.9	8.3 ± 0.8	22.3 ± 1.5	38.2
MEK	1.7 ± 1.2	1.3 ± 0.6	9.3 ± 2.1	22.0 ± 2.6	34.3
WES	2.0 ± 1.0	1.3 ± 0.6	8.3 ± 2.1	16.7 ± 6.7	28.3
BID	1.7 ± 0.6	1.0 ± 1.0	6.0 ± 1.0	13.0 ± 1.0	21.7
GDA	1.3 ± 0.6	1.0 ± 1.0	2.7 ± 1.2	6.7 ± 1.2	11.7
GIU	1.3 ± 0.6	1.3 ± 0.6	1.7 ± 0.6	4.7 ± 1.5	9.0
HVA	0.7 ± 0.6	0.5 ± 0.5	6.8 ± 0.8	3.9 ± 1.0	11.9
ASKO	1.0 ± 0.0	1.0 ± 1.0	1.7 ± 0.6	3.3 ± 0.6	7.0
ORI	0.7 ± 0.6	0.7 ± 0.6	2.0 ± 1.0	2.3 ± 1.5	5.7
GRE	0.7 ± 0.6	0.3 ± 0.6	1.3 ± 0.6	2.7 ± 0.6	5.0
CRI	7.0 ± 0.9	0.0 ± 0.0	0.0 ± 0.0	1.2 ± 0.1	8.2
CON	2.0 ± 3.5	0.0 ± 0.0	0.0 ± 0.0	1.3 ± 2.2	3.3
RE	0.0 ± 0.0	0.0 ± 0.0	1.2 ± 2.1	2.6 ± 2.2	3.8
MAR	0.3 ± 0.6	0.0 ± 0.0	0.0 ± 0.0	0.3 ± 0.6	0.6

High concentrations of PCBs were also found in *M. edulis* collected at the Icelandic REY site in the fishing harbor of Reykjavik (sum of all PCBs 38.2 ng g^{-1} DW, mean rank 4.6). Organic compounds derived from anthropogenic pollution are considered unusual in the relatively pristine coastal waters of Iceland since there is little industry in this region and the country is located far from other potential sources of pollution. Thus, it is hypothesized that organic contaminants from lower latitudes are transported over long distances towards this subarctic area, as it is also suggested by Wania and Mackay (1993), Burkow and Kallenborn (2000) and Hoekstra et al. (2003). Another plausible explanation of high PCB
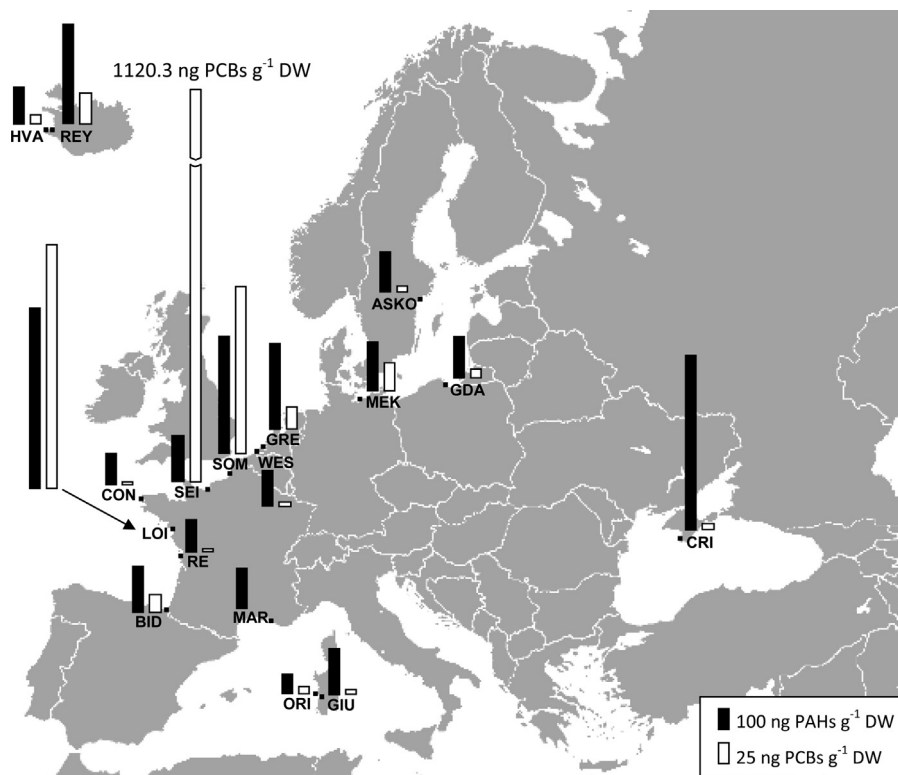
Figure 2 Sum of concentrations of PCBs and PAHs (adjusted with SVC) in soft tissues of *Mytilus* spp. [ng g^{-1} DW] at 17 sites in the European coastal waters.

concentration at the REY site includes dredging in the commercial port between 2002 and 2003 (*Mannvit Engineering* internet data) which could release PCBs deposited in the sediments into the water column and the subsequent bioaccumulation in mussels. Indeed, another Icelandic site — HVA, which is located several kilometers to the south of Reykjavik, showed much lower accumulated concentrations of PCBs (a sum of all PCBs 11.9 ng g^{-1} DW, mean rank 10.8).

Relatively high levels of PCBs were documented in mussels at the WES site in the Westerschelde estuary (28.3 ng g^{-1} DW; mean rank 6.0) and at the MEK site in Mecklenburg Bay (34.3 ng g^{-1} DW; mean rank 5.9). According to recent studies on the Dutch delta area, Westerschelde is the most polluted region of the Dutch coast with concentrations of PCBs in *Mytilus* spp. ranging from 200 ng g^{-1} DW to even 750 ng g^{-1} DW (Hummel et al., 1990). Conversely, at GRE (in the Grevelingen Meer), another Dutch site, PCB concentrations were much lower (5.0 ng g^{-1} DW, mean rank 13.0) which concurs with previous observations of Hummel et al. (1990) who also reported lower PCB levels in the soft tissues of mussels from this area. Since the bivalves used in the current study were sampled from exactly the same site as those collected in the 1980s (Hummel H., personal communication), it was possible to make an initial historical comparison. Comparing the data from Hummel et al. (1990) with those collected in the present study indicates that there is a noticeable decrease in PCB concentrations in the Westerschelde estuary, while a similar decreasing trend was also noted in other geographical regions (Stephenson et al., 1995; van Metre and Wilson, 1998). Elevated soft tissue PCB concentrations in mussels from Mecklenburg Bay (MEK) correspond well with the high levels of these compounds in sediments (Dannenberger and Lerz, 1996; Schiedek et al., 2006). While the primary sources of chlorinated hydrocarbons are the shipbuilding industry, shipping operations, agriculture, and urban effluents, it cannot be excluded that PCBs are introduced into Mecklenburg Bay in a form that is bound to organic suspended matter of riverine origin from the Oder and Penne, large rivers located further to the east (Dannenberger and Lerz, 1996).

The accumulated PCB concentrations in mussels from the Gulf of Gdańsk (GDA, 11.7 ng g^{-1} DW, mean rank 9.1) were similar to those reported earlier by Potrykus et al. (2003) (10.0 ng g^{-1} DW, using a wet weight to dry weight conversion factor after Riccardi and Bourget (1999)). The main sources of PCBs in the coastal waters of the Polish part of the southern Baltic Sea are the Vistula River and the large industries located in Gdynia and Gdańsk (shipyards, oil refineries, chemical factories, fishery, sewage treatment plants). Rank comparison shows that soft tissue levels of PCBs similar to those in the Gulf of Gdansk were observed at the BID, GIU, HVA, ASKO, and ORI sites at mean ranks ranging from 8.1 to 12.3. These similarities, however, might not result only from the similar total concentrations of PCBs present, but might also be an effect of different salinity. At the CRI site in the Blue Bay of the Black Sea, the total PCB concentrations in *Mytilus galloprovincialis* were considered low (8.2 ng g^{-1} DW, mean rank 13.5). Although the Blue Bay is a narrow lagoon situated close to a heavily industrialized area of Sevastopol, the jagged shoreline and sea current patterns in this area likely restrict the distribution of PCBs to the harbor and the open waters of Sevastopol Bay, which

effectively reduces direct transport of them to neighboring bays. Another site characterized by relatively low PCB levels was the CON site on the westernmost edge of Brittany where concentrations in mussels reached 3.3 ng g^{-1} DW (mean rank 13.9), which is only slightly lower than those reported by Bodin et al. (2007) (8.9 ng g^{-1} DW). The roadstead of Brest, a large urban area with various industries and a large naval base, is a source of PCBs in the coastal waters of this part of France (Bodin et al., 2007).

The lowest PCB concentrations were found in bivalves at the RE site on the French Atlantic coast (sum of all PCBs 3.8 ng g^{-1} DW, mean rank 15.3) and the MAR site in the Mediterranean Sea (0.6 ng g^{-1} DW, mean rank 16.8). The RE site is located at Rivedoux in the eastern part of the island Ile de Ré close to La Rochelle, a large city with a population of about 80,000, a commercial port, and a yacht harbor. According to Roméo et al. (2003), PCB concentrations in mussels collected in the Bay of La Rochelle in June 1999 was 292.25 ng g^{-1} DW. In the current study, the PCB concentration in mussels was only 3.8 ng g^{-1} DW, which is more than 81-fold lower, which suggests the reduced input of polychlorinated biphenyls into the coastal system in recent years. A consistent trend of decreasing PCB concentration since the end of the 1970s has been also observed at the MAR site, which was the least polluted with PCBs (sum of all PCBs 0.6 ng g^{-1} DW; mean rank 16.8). Villeneuve et al. (1999) found the PCB concentration (expressed as the Aroclor 1254 equivalent) in mussel soft tissues collected in 1988/1989 near Marseille to be nearly six-fold lower than those in 1975 (520 ng g^{-1} DW for the sum of PCB congeners 101, 138 and 153).

4.2.2. Polycyclic aromatic hydrocarbons

Distinct, large-scale geographical variations were also noted in concentrations of polycyclic aromatic hydrocarbons along the European coast (Fig. 2, Table 8). Naphthalene and phenanthrene occurred in the highest concentrations at most sites, except at the Black Sea CRI site where the dominant compound was benzo(a)pyrene. Naphthalene and phenanthrene contribute most to total PAH concentrations in mussel soft tissues in these areas with the percentage contribution ranging from 36.1% to 90.9%.

High accumulated total PAH concentrations were found in bivalves at the LOI, CRI, SOM, and REY sites (Table 8). Except for the REY and CRI sites, high pollution levels in these areas result from elevated naphthalene concentrations which exceed concentrations of other compounds several-fold (Table 8). Markedly raised levels of naphthalene in the Loire River estuary (LOI) is presumably from the prolonged impact of the ecological disaster that ensued after the wreck of the Maltese oil tanker *Erika* and the resulting oil spill in December 1999. This event affected the entire northern French Atlantic Coast from Finistère to the mouth of the Loire River (Poncet et al., 2000). The simultaneous increase of PAHs concentrations in the water and suspended matter indicates that the contamination of this region is serious and persistent (Tronczyński et al., 2004). It also cannot be excluded that the Loire River is an important source of bioavailable PAHs in the coastal zone as is the Somme River in the southern English Channel (SOM; Amara et al., 2007) and the Scheldt River in the Westerschelde estuary (WES).

Table 8 Concentrations of PAHs (adjusted with SVC) in soft tissues of *Mytilus* spp. [ng g^{-1} DW] from the European coastal waters (nd — below LOD or LOQ). For PAHs abbreviations see Table 2.

Site	Nap	Phe	An	Flu	Py	B[a]An	Chr	B[b]Flu	B[k]Flu	B[a]Py	B[g,h,i]Pe	Σ
HVA	nd	72.8 ± 4.2	3.2 ± 0.5	44.6 ± 8.8	34.7 ± 3.3	0.3 ± 0.4	0.8 ± 0.7	10.3 ± 2.3	7.0 ± 1.7	12.5 ± 2.3	nd	186.2
REY	nd	178.5 ± 9.0	10.7 ± 1.4	92.8 ± 14.1	98.4 ± 10.8	17.4 ± 3.1	35.3 ± 4.0	24.0 ± 3.4	16.0 ± 1.0	21.5 ± 3.8	nd	494.6
ASKO	45.7 ± 4.2	82.0 ± 7.0	8.7 ± 2.5	14.0 ± 2.6	9.3 ± 0.6	5.7 ± 1.5	12.7 ± 2.5	9.7 ± 2.5	7.0 ± 1.0	2.7 ± 1.5	2.7 ± 2.1	200.2
GDA	10.7 ± 2.1	114.7 ± 7.2	9.3 ± 1.2	18.7 ± 2.1	15.7 ± 2.1	5.3 ± 3.1	7.0 ± 2.6	6.7 ± 1.2	5.0 ± 1.0	6.0 ± 1.0	6.7 ± 1.2	205.8
MEK	61.3 ± 5.5	87.7 ± 4.7	9.3 ± 0.6	23.3 ± 3.5	19.0 ± 2.0	8.0 ± 1.0	13.3 ± 1.5	9.3 ± 1.5	6.7 ± 0.6	3.0 ± 1.0	4.3 ± 1.2	245.2
GRE	41.7 ± 3.5	74.3 ± 4.7	5.7 ± 0.6	16.0 ± 1.7	11.0 ± 1.0	4.3 ± 0.6	6.0 ± 1.0	6.0 ± 1.0	4.3 ± 1.2	2.7 ± 0.6	5.0 ± 1.0	177.0
WES	294.3 ± 6.7	57.0 ± 1.7	3.3 ± 1.5	23.3 ± 1.5	13.0 ± 2.0	3.3 ± 1.2	7.7 ± 1.2	10.3 ± 2.1	3.3 ± 0.6	4.0 ± 0.0	3.7 ± 1.5	423.2
SOM	473.0 ± 3.4	54.5 ± 0.0	1.9 ± 1.0	26.7 ± 0.9	11.2 ± 3.0	1.9 ± 0.6	2.6 ± 0.7	2.7 ± 0.3	0.8 ± 0.5	2.6 ± 0.2	0.9 ± 0.0	578.8
SEI	nd	108.3 ± 0.0	3.8 ± 0.8	28.9 ± 0.8	19.9 ± 3.5	9.7 ± 1.5	10.1 ± 0.8	19.2 ± 1.5	6.2 ± 1.2	15.1 ± 0.9	5.1 ± 0.0	226.3
CON	34.0 ± 9.3	72.5 ± 0.0	1.7 ± 0.7	26.7 ± 0.5	10.9 ± 3.7	2.1 ± 0.7	2.0 ± 0.4	3.1 ± 0.6	1.0 ± 0.5	2.6 ± 0.2	nd	156.6
LOI	815.7 ± 42.8	47.3 ± 0.0	1.6 ± 1.3	13.8 ± 0.5	6.4 ± 1.9	2.0 ± 0.8	2.0 ± 0.4	3.7 ± 0.8	1.2 ± 0.4	3.3 ± 0.5	0.6 ± 0.0	897.6
RE	61.5 ± 11.3	63.7 ± 0.0	2.9 ± 0.6	14.7 ± 0.5	6.6 ± 2.8	1.3 ± 0.6	1.8 ± 0.5	2.4 ± 0.5	0.8 ± 0.4	1.8 ± 0.2	0.6 ± 0.0	158.1
BID	98.7 ± 4.0	87.7 ± 7.0	4.0 ± 1.0	13.7 ± 3.1	7.3 ± 0.6	4.7 ± 0.6	3.3 ± 1.2	4.0 ± 1.0	3.0 ± 1.0	1.7 ± 0.6	2.0 ± 1.0	230.1
MAR	17.0 ± 3.6	82.3 ± 7.8	7.3 ± 1.2	7.7 ± 0.6	7.7 ± 1.5	1.7 ± 0.6	2.0 ± 1.0	1.7 ± 0.6	1.3 ± 0.6	70.0 ± 4.6	1.7 ± 0.6	200.4
ORI	84.3 ± 6.0	99.3 ± 9.7	4.7 ± 1.2	13.7 ± 1.5	10.0 ± 2.6	2.0 ± 1.0	2.7 ± 1.2	2.0 ± 1.0	1.7 ± 0.6	2.0 ± 1.7	1.7 ± 0.6	224.1
GIU	nd	65.7 ± 3.8	2.3 ± 1.5	13.3 ± 2.1	7.3 ± 2.1	2.7 ± 0.6	0.7 ± 0.6	1.0 ± 1.0	0.7 ± 0.6	1.0 ± 0.0	nd	94.7
CRI	94.7 ± 2.2	135.9 ± 5.2	6.9 ± 1.3	17.5 ± 1.4	30.2 ± 2.5	15.3 ± 1.9	19.4 ± 1.8	5.5 ± 0.9	4.6 ± 1.1	536.7 ± 107.0	nd	866.7

With regard to other compounds (except Nap), the highest PAH levels were noted at the REY site in Reykjavik harbor (494.6 ng g^{-1} DW, mean rank 4.1), which was also highly ranked for PCBs. This corroborates the results of Skarphédinsdóttir et al. (2007) from a location situated near the urbanized area of Grafarvogur (5 km from Reykjavík) where concentrations of PAHs in mussels reached 560 ng g^{-1} DW. The calculated ratios of Flu/Py and Phe/An indicate that the origin of PAHs is mostly petrogenic and a probable source of contamination is the Reykjavik harbor (Fig. 3). Highly ranked sites also included MEK, SEI, CRI, and GDA (mean rank from 5.3 to 6.0). According to Witt (1995), Mecklenburg Bay is considered to be one of the western Baltic regions with the highest PAH pollution. The hypothesis is that the PAHs here originate from central Europe and are transported bound to suspended particulate matter along the coast over long distances. In contrast, the urbanized, industrialized areas of the Seine River drainage area are thought to be the principal source of PAHs at the SEI site. Additional PAH input might originate from one of the largest commercial trade ports in Europe and the large oil refinery located in the Seine estuary. This is supported by the high Phe/An and Flu/Py ratios that are indicative of both: the petrogenic and pyrolitic origin of polycyclic aromatic hydrocarbons. The petrogenic character of PAHs was also noted at the CRI site in the Black Sea, which is also severely polluted (Fig. 3), and where mussel soft tissues contained exceptionally high levels of carcinogenic benzo(a)pyrene (536.7 ng g^{-1} DW). Elevated concentrations of B[a]Py in coastal waters can suggest, however, the combustion of organic material (including coal, automobile exhaust fumes, and charbroiled foods) as a supplementary source of PAHs. At the GDA site, Potrykus et al. (2003) reported PAH concentration data for *M. edulis/trossulus* collected in 1997 in the same area as that examined in the present study. These two data sets can therefore be compared to identify inter-year differences, and they can serve to highlight the power of biomonitoring programs for tracking change over long periods. The historical comparison of PAHs indicated there was a several-fold increase in concentrations in bivalves in recent years. One possible explanation could be gas emissions from the sewage sludge incinerator at the nearby Dębogórze Water Treatment Plant located in
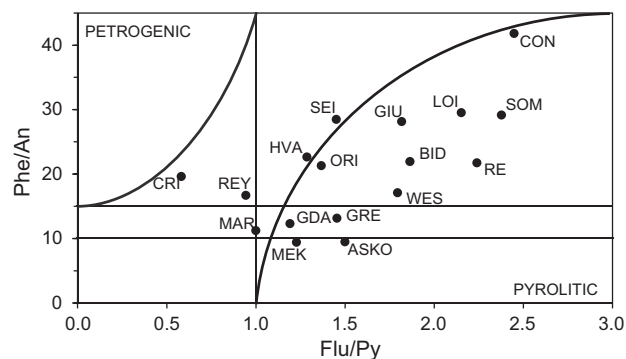

Figure 3 Plot of ratios phenathrene/anthracene (Phe/An) against fluoranthene/pyrene (Flu/Py) in mussels from 17 sampling sites. Pyrolitic PAHs: Phe/An < 10 and Flu/Py > 1; petrogenic PAHs: Phe/An > 15 and Flu/Py < 1.

the coastal zone of the Gulf of Gdańsk. The incinerator began operations in 1998 and currently burns 70–80 t of organic sewage matter per day (Dębogórze WTP data). The Phe/An and Flu/Py ratios indicative of the pyrolitic origin of the PAHs support this hypothesis (Fig. 3).

The ASKO site located in the Trosa Archipelago in the central Baltic Sea exhibited intermediate PAH contamination (200.2 ng g^{-1} DW, mean rank 7.2), which does not reflect previous low results (40 ng g^{-1}) found in this location by Skarphédinsdóttir et al. (2007). Low Phe/An and Flu/Py ratios indicate the pyrolitic origin of PAHs, which are thought to come from remote locations with atmospheric transport. Similar PAH levels in *M. edulis* were measured at the Dutch GRE (177.0 ng g^{-1} DW; mean rank 8.3) and WES (423.3 ng g^{-1} DW; mean rank 7.5) sites. In the Westerschelde estuary of the Scheldt River, the extended salt marshes and tidal flats serve as a sedimentation platform for organic matter and a reservoir of organic pollutants from upstream. The major local source of PAHs certainly includes the Antwerp harbor that is located on both sides of the river and is one of the largest ports in Europe. Sediments are also thought to be the main source of PAHs in the brackish Grevelingen Lake (GRE, mean rank 8.3), which is the former Rhine-Meuse estuary. Currently, the lake has a very limited connection with the river system which substantially reduces suspended matter sedimentation. Intermediate concentrations of PAHs were also found in mussels from the Icelandic HVA site (186.2 ng g^{-1} DW, mean rank 9.5). A relatively pristine region of Hvassahraun is located away from industrial centers and shipping routes; therefore, it is used as a reference site in Icelandic monitoring programs (Halldórsson et al., 2005).

The concentrations of PAHs noted at the BID site in the Bidasoa estuary (230.1 ng g^{-1} DW; mean rank 9.8) contrast with those reported in mussels collected from the same area in 2004 (1194.0 ng g^{-1} DW) by Bartolome (2007). He explained high concentrations of PAHs as the result of the heavy-oil spill that followed the sinking of the tanker *Prestige* that sank in Galician waters off of the northwest coast of Spain in November 2002. Our results don't support this assumption. Also, the high Phe/An and Flu/Py ratios indicate the mixed pyrolitic/petrogenic origin of these pollutants, so other sources certainly contribute to the elevated PAH concentrations in mussels.

Much lower soft tissue PAH concentrations were measured at the Mediterranean sites of ORI (224.1 ng g^{-1} DW) in the Gulf of Oristano and at MAR (Marseille, 200.4 ng g^{-1} DW) as well as at SOM (578.8 ng g^{-1} DW) on the French coast of the English Channel (mean rank from 10.5 to 11.0). The Gulf of Oristano borders the western part of Sardinia and its only industry is a small commercial port located near the Triso River which discharges freshwater into the gulf (Magni et al., 2006). The levels of PAHs recorded in mussels from Marseille (200.4 ng g^{-1} DW) correspond well with the decreasing trend of PAH concentrations in this area over the last 20 years. Villeneuve et al. (1999) reported accumulated soft tissue concentrations of these compounds in 1988/1989 of 353 ng g^{-1} DW (sum of acenaphthene, anthracene, pyrene, phenanthrene, fluorene, and fluoranthene) while Baumard et al. (1998) reported only 305.0 ng g^{-1} DW in 1995.

Decreased concentrations of PAHs were also noted in bivalves from the CON site of the Iroise Sea coast near Le Conquet in Western Brittany (156.6 ng g^{-1} DW, mean rank 12.1). The village Le Conquet and the surrounding area are sparsely populated and the principal local activity is agriculture. Organic pollutants in coastal waters likely derive from maritime traffic, including important shipping routes across the Iroise Sea (Muller et al., 2009). High ratios of Phe/An and Flu/Py (Fig. 3) indicate that PAHs originate from both petrogenic and pyrolitic sources. A similar total PAH concentration (158.1 ng g^{-1} DW, mean rank 13.5) was found at the RE site on the eastern coast of Ile de Ré next to the large city of La Rochelle. Previous studies by Roméo et al. (2003) revealed higher concentrations of the sum of PAHs (up to 209.14 ng g^{-1} DW) in mussels in 1999. Phe/An and Flu/Py ratios indicate that the PAHs are of both petrogenic and pyrolitic origin. The lowest observed concentrations of PAHs occurred in *M. galloprovincialis* at the GIU site in the Santa Giusta Lagoon (94.7 ng g^{-1} DW, mean rank 15.4), which is a shallow (mean depth 1 m), inland lagoon separated from the sea by a wide sandbar with two canals connecting the lagoon with the open sea and the nearby industrial harbor (Sechi et al., 2001). The low concentration of PAHs in these mussels reflect low concentrations of these compounds in the sediments of Santa Giusta Lagoon that range from 3.8 ng g^{-1} DW to 250.9 ng g^{-1} DW (Specchiulli et al., 2010). Probably most PAHs come into the lagoon with surface runoff from the nearby cities of Oristano and Santa Giusta and from the industrial harbor.

5. Conclusions

Comparisons of large-scale monitoring show that there are geographical variations in the concentrations of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in different regions along the European coastline. This study provides a benchmark against which future biomonitoring programs will be able to trace changes in PCB and PAH pollution in coastal ecosystems. Using mussels from the *M. edulis* complex as biomonitors allowed measuring the bioavailable (i.e., ecologically important) fraction of these chemicals that can potentially cause ecotoxicological effects and biomagnify in the food chain. High concentrations of PCBs and PAHs were generally recorded in the estuaries of large rivers and in the vicinity of industrial and urban centers. This highlights the significance of both terrestrial input and human activity in coastal areas as sources of bioavailable organic contaminants in coastal and estuarine regions. Although the production of PCBs was stopped over 30 years ago, their biogeochemical release from sediments means they remain ubiquitous in the marine environment, particularly in extended organic-rich tidal flats, which underlies the importance of local sources. In the case of PAHs, oil spills from shipwrecks and refineries can contribute significantly to elevated pollution levels on local scales. Due to their persistence and low solubility, PCBs and PAHs can also be transported long distances, which is why they are found at remote locations that are considered to be pristine, i.e., sites in Iceland. In addition to geographical differences in PCB and PAH concentrations, long-term changes were noted at some sites, which indicates decreasing trends in PCB levels in coastal zones in recent years.

Acknowledgments

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