



Vertical profiles of sedimentary polycyclic aromatic hydrocarbons and black carbon in the Gulf of Gdańsk (Poland) and Oslofjord/Drammensfjord (Norway), and their relation to regional energy transitions

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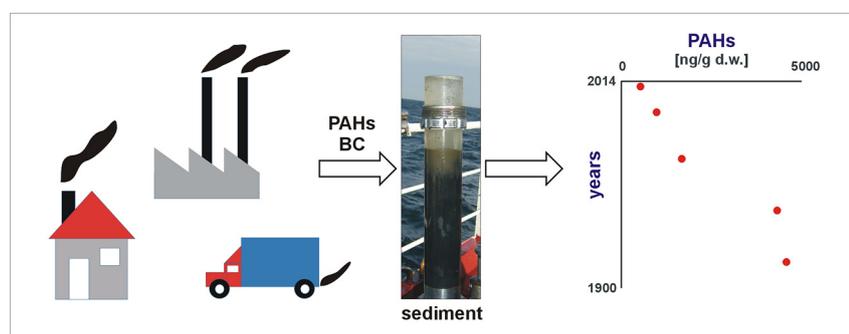
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HIGHLIGHTS

- Dated sediments can be used for reconstructing anthropogenic emissions.
- Temporal PAH trends in Gulf of Gdańsk and Norwegian fjords reflect their energy sources.
- The transition from fossil fuel combustion to hydropower was evident in the fjords.
- Restrictions on using solid fuels in residential heating reduce PAH emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

The analysis of undisturbed sediment cores is a powerful tool for understanding spatial and temporal impacts of anthropogenic emissions from the energy and transport sectors at a regional scale. The spatial and vertical distribution of polycyclic aromatic hydrocarbons (PAHs) and black carbon (BC) were determined in 12 cores of recent (up to 20 cm long) sediments from the Gulf of Gdańsk in Poland, and Oslofjord/Drammensfjord in Norway. The $\Sigma 12$ PAHs levels in individual sediment layers varied from 250 to 4500 ng/g d.w. in the Gulf of Gdańsk, and from 210 to 4580 ng/g d.w. in the Norwegian fjords. Analysis of PAH ratios indicates that PAHs in both studied areas originated mainly from pyrogenic sources. The BC concentrations in sediments were up to 0.9% and were generally higher in the Gulf of Gdańsk (mean - 0.39%) than in Oslofjord/Drammensfjord (mean - 0.19%). The deposition history of anthropogenic emissions over the last 100 years was reconstructed based on the analysis of dated and well-laminated sediment cores from two stations from the Gulf of Gdańsk and two stations from the Norwegian fjords. The evolution in energy structure was especially evident in the Oslofjord, where transition from fossil fuel combustion to hydropower after 1960 coincided with a sharp decrease in sedimentary PAHs. Despite significant changes in the economic development in Poland, temporal patterns in PAH concentrations/profiles in the Gulf of Gdańsk were not as obvious. The historical PAH trends in the Gulf of Gdańsk may be related to the overwhelming PAH inputs from domestic combustion of solid fuels (coal, wood) for heating purposes. The implementation of

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legislation and other activities addressed to restrict the use of solid fuels in residential heating should reduce PAH emissions.

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1. Introduction

There is general consensus that the Earth has undergone and is undergoing significant changes linked to anthropogenic impact. Some scientists suggest using the term 'Anthropocene' to describe the present epoch, in which many key environmental processes are influenced by human activities (Crutzen and Stoermer, 2000; Irabien et al., 2015). These anthropogenic pressures are reflected in levels of chemicals that have been documented in various environmental matrices, including sediments that preserve the record of pollution over time (Heim and Schwarzbauer, 2013). Thus, well-laminated sediments in depositional areas, where post-depositional processes of bioturbation, pore-water transport and biotransformation are absent or negligible, function as 'chemical archives' that provide insights into the history of past anthropogenic activities (Cantwell et al., 2007; Gevaio et al., 2016).

Various sediment markers document human activities in an anthropogenic climate change context. For example, the historical evolution of emissions such as polycyclic aromatic hydrocarbons (PAHs) is mainly influenced by changes in economic activities, domestic heating, energy production, transport as well as environmental legislation (Foan et al., 2010). Profiles of indicators, including PAHs and black carbon (BC) in dated sediments also offer the possibility of reconstructing the spatial and temporal trends of pollutant emissions and may reflect changes in fossil fuel and energy sources (Arp et al., 2011). For example, Leorri et al. (2014) investigated sediments from northern Spain and reconstructed the human impact over the last 700 years. These investigations suggest that atmospheric emissions from coal used by regional metallurgic industry increased in the early 1800s and the highest emissions associated with leaded gasoline peaked in 1975. Similar correlations are also documented in sedimentary records from different regions in China (Hu et al., 2011; Cai et al., 2016; Li et al., 2015; Liu et al., 2005). In many developed countries anthropogenic PAHs reached maximum values in the period from 1950s to 1960s or 1980s (depending on location) and decreases of PAHs could be mainly attributed to the transitions in energy structure (Guo et al., 2010; Li et al., 2015; Lorgeoux et al., 2016). These studies highlight differences in transitions in energy structure and subsequently economic development at the regional scale.

Spatial scale is important when investigating the impact of energy sources and case specific studies provide a useful reference at the regional scale. To further explore the anthropogenic impact of energy sources at the regional scale, this study is exploring the sedimentary record of PAHs and BC in two different European marine coastal areas adjacent to urbanized areas, in the Gulf of Gdańsk, Poland as well as in Oslofjord and Drammensfjord in Norway. The investigations focus on anthropogenic inputs from the late 1800s/early 1900s with the objective to document human impacts at the regional scale, investigate temporal and spatial correlations to understand potential transitions in energy structure and subsequently reflect on the implementation of legislation to reduce anthropogenic inputs.

2. Materials and methods

2.1. Geographic characteristics of the study areas

This study focus on two different European marine coastal areas: the Gulf of Gdańsk (Poland) and the Oslofjord/Drammensfjord (Norway) (Fig. 1). Both basins have limited deeper-water exchange and have been previously described in detail by Szymczak-Żyła et al. (2017).

Briefly, the Gulf of Gdańsk is located in the southern part of the Baltic Sea. This basin is under strong anthropogenic impact as a result of the proximity of industrial activities and the densely populated Gdańsk-Sopot-Gdynia conurbation (>1.2 million inhabitants). Furthermore, the Gulf is influenced by the River Wisła (Vistula), which catchment area covers about 54% of the territory of Poland and is inhabited by almost 60% of the country's population. Subsequently, the Gulf of Gdańsk is impacted by various anthropogenic stressors related to industrial, traffic, municipal and agriculture effluents.

The Oslofjord is a part of Skagerrak strait. The Oslofjord lies in the vicinity of Oslo agglomeration, an area that has undergone transformation from earlier industrial activities to urbanization and currently is the most populated (>1.4 million inhabitants) area in Norway. The outer Oslofjord is connected to the Drammensfjord, which is strongly influenced by River Drammen. The River Drammen runs through the centre of the city of Drammen, which is much smaller than Oslo but with a relatively large harbour area. Since the 1800s, the influx of organic material to Drammensfjord has increased as a consequence of the pulp and paper industry, and an increasing population and more intensive agriculture in the river basin area.

2.2. Sampling and characteristics of sampling stations

Cores of recent sediments were taken during two sampling campaigns of r/v 'Oceania' at six stations in the Gulf of Gdańsk (April 2014) in Poland and at six stations in the Oslofjord/Drammensfjord (June 2014) in Norway (Fig. 1). The sampling sites were selected so as to represent different exposure to contamination and different environmental conditions in the study areas, i.e. different water depth, salinity, oxic conditions, type of sediment, distance from the coastline and potential pollution sources. Sediment samples were collected with a Niemistö core sampler in the Gulf of Gdańsk and with a GEMAX twin-core sampler in the Norwegian fjords. Each of the 12 sediment cores was divided into the following layers: 0–1, 1–5, 5–10, 10–15 and 15–20 cm. At sites BMPK10 and P104 only 10 cm long cores were sampled due to the hard bottom (high content of sand fraction). All the sediment samples were frozen on board immediately after collection.

Some physicochemical parameters of near-bottom water and sediments at the sampling sites are presented in Table 1 and a detailed description of the study areas was presented in Szymczak-Żyła et al. (2017). Briefly, the Norwegian fjords were characterised by higher salinity compared to the Gulf of Gdańsk. Low levels of dissolved oxygen in near-bottom water were reported at most sites. Sediments varied from silty sand at stations BMPK10 and P104 to silt and clayey silt at other stations. The sediment samples from the northern part of the Gulf of Gdańsk had the highest concentrations of organic matter. Sediment accumulation rates were determined based on Pb-210 activity concentration profiles and were found to vary from 0.05 to 0.27 cm/yr.

2.3. Dated sediment cores for reconstructing historical trends

Dated sediment cores have been widely used to reconstruct the history of emissions in relation to past human activities (Bigus et al., 2014). In our study, two sediment cores from the Gulf of Gdańsk (P1, P116), one from the Drammensfjord (B) and one from the Oslofjord (E) were selected for investigating temporal emission trends of PAHs and BC from the late 1800s/early 1900s. The mean annual fluxes of $\Sigma 12$ PAHs were calculated for averaged 0–5 cm sediment layer and deeper layers taking into account sediment accumulation rates reported by

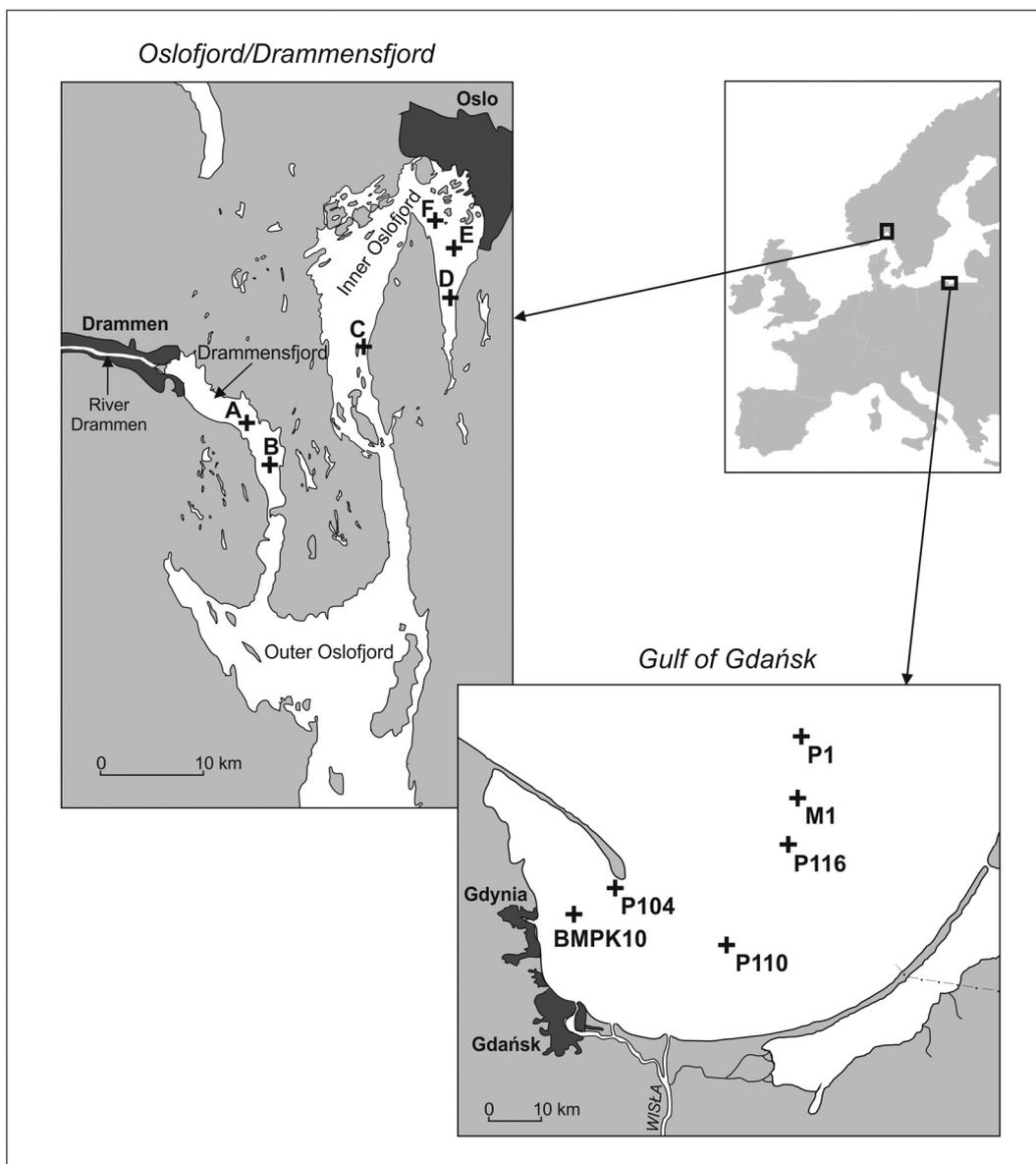


Fig. 1. Study areas: Gulf of Gdańsk and Oslofjord/Drammensfjord.

Szymczak-Żyła et al. (2017). The sediments from these four stations were well-laminated based on Pb-210 analysis (Szymczak-Żyła et al., 2017). Furthermore, environmental conditions at all these stations may enhance the persistence of pollutants buried in sediments, mainly due to oxygen depletion, lack of sunlight and limited biological activity. As contents of organic carbon and the fine grain-size fraction (<63 μm) were comparable in each of the sediment layers for each of the cores studied, we may assume that differences between concentration levels for the sediment layers could be mainly related to variation in emission inputs, and not to differences in the sedimentary environment. Thus, these well preserved sedimentary records should provide reliable insight into the history of anthropogenic emissions in the studied water bodies.

2.4. Determination of PAHs, TOC and BC

PAHs were extracted from sediments and analysed using GC/MS according to the procedure used by Lubecki and Kowalewska (2010) with some modifications (Supplementary information, S1).

Total organic carbon (TOC) analyses were carried out using a Flash EA 1112 Series Elemental Analyzer combined with an IRMS Delta V Advantage Isotopic Ratio Mass Spectrometer (Thermo Electron Corp., Germany). The detailed procedure is described elsewhere (Szymczak-Żyła et al., 2017).

The BC concentration of the dried sediment samples was determined at the Norwegian University of Life Sciences, using the chemothermal oxidation method (CTO-375) as described by Gustafsson et al. (1997) where combustion at 375 °C creates a combusted sediment with only BC and no other organic matter remaining. A small sample of dry sediment (10 mg in Ag capsules) was first heated at 375 °C during 18 h under a constant air flow of 200 ml/min. BC was quantified using the same procedure as for TOC.

2.5. Statistical analysis

The results were statistically processed using Microsoft Office Excel and STATISTICA 6.0 software. The following statistical methods were

Table 1
Characteristics of the sampling stations from the Gulf of Gdańsk and Oslofjord/Drammensfjord.

| Station | Water depth [m] ^a | Parameters of near-bottom water ^a | | | Parameters of sediments | | | | | |
|-------------------------|------------------------------|--|----------|---------------|--|--------------------------------|--------------------------------|----------------------|----------------------------------|------------|
| | | Temp. [°C] | Salinity | Oxygen [mg/L] | Accumulation rate [cm/yr] ^a | Mixing depth [cm] ^a | <0.063 mm fr. [%] ^a | TOC [%] ^a | BC [%] | BC/TOC [%] |
| Gulf of Gdańsk | | | | | | | | | | |
| P1 | 112 | 6.3 | 12.0 | 3.4 | 0.16 ± 0.01 | 0 | 99.2–100 | 4.22–8.13 | 0.40–0.88 (0.52) ^b | 8.0–10.8 |
| M1 | 95 | 6.4 | 11.7 | 3.9 | 0.16 ± 0.01 | 0 | 100 | 4.50–6.90 | 0.43–0.85 (0.53) ^b | 7.1–12.3 |
| P116 | 92 | 6.4 | 10.8 | 0.5 | 0.14 ± 0.01 | 0 | 100 | 5.65–7.52 | 0.45–0.82 (0.54) ^b | 7.1–11.4 |
| P110 | 72 | 5.0 | 8.6 | 5.4 | 0.17 ± 0.02 | 3 | 97.3–99.2 | 4.89–6.65 | 0.32–0.49 | 5.7–7.7 |
| BMPK10 | 31 | 4.9 | 7.5 | 11.1 | – ^c | 12 | 20.3–46.1 | 1.06–3.36 | 0.09–0.15 | 4.2–10.3 |
| P104 | 55 | 4.5 | 7.6 | 12.1 | – ^d | 12 | 27.8–35.9 | 1.02–2.77 | 0.06–0.24 | 2.1–14.8 |
| Oslofjord/Drammensfjord | | | | | | | | | | |
| A | 113 | 8.0 | 31.2 | 0.3 | 0.11 ± 0.01 | 0 | 99.2–100 | 1.57–2.48 | 0.12–0.28 | 5.8–12.6 |
| B | 122 | 8.2 | 31.0 | 0.5 | 0.27 ± 0.02 | 0 | 100 | 1.35–1.98 | 0.09–0.26 | 5.5–13.8 |
| C | 156 | 8.3 | 32.3 | 9.2 | 0.20 ± 0.02 | 4 | 100 | 2.33–2.97 | 0.13–0.35 | 5.2–12.0 |
| D | 152 | 9.2 | 32.6 | 1.7 | 0.10 ± 0.03 | 5 | 100 | 2.58–3.85 | <0.1–0.14 | 1.3–5.0 |
| E | 77 | 8.5 | 33.2 | 0.2 | 0.18 ± 0.01 | 0 | 100 | 1.58–4.39 | 0.19–0.32 | 5.0–12.0 |
| F | 78 | 8.3 | 33.6 | 1.7 | 0.05 ± 0.01 | 3 | 100 | 1.61–6.20 | 0.14–0.26 | 4.2–8.7 |

Abbreviations: Temp. – temperature; <0.063 mm fr. – <0.063 mm grain-size fraction; TOC – total organic carbon; BC – black carbon.

^a Based on Szymczak-Żyła et al. (2017).

^b In brackets given maximal values if top (0–1 cm) sediment layers not taken into account (due to possible charring these samples when using CTO-375 method).

^c No accumulation or max 0.07 ± 0.01.

^d No accumulation.

applied: Shapiro-Wilk test, Mann–Whitney *U* test, cluster analysis, linear regression model.

3. Results and discussion

3.1. Distribution and origin of PAHs

The concentrations of PAHs in individual sediment layers (i.e. 0–1, 1–5, 5–10, 10–15, 15–20 cm) from the Gulf of Gdańsk and Oslofjord/Drammensfjord are provided in the Supplementary information (Table S2.1). The concentrations of sum of 12 parent PAH compounds ($\Sigma 12$ PAHs) were found to vary from 250 (P104, 1–5 cm) to 4500 ng/g (P116, 10–15 cm) in the Gulf of Gdańsk, and from 210 (B, 0–1 cm) to 4580 ng/g (E, 15–20 cm) in the Norwegian fjords (Fig. 2). The differences between the mean $\Sigma 12$ PAHs concentrations in the Gulf of Gdańsk and Oslofjord/Drammensfjord were not statistically significant (Mann–Whitney *U* test, $p > 0.05$). The elevated PAH contents in the Gulf of Gdańsk were reported in its northern part, which is called Gdańsk

Deep and acts as a major depositional area for suspended particulate matter and their associated contaminants. The lowest concentrations of PAHs in the Gulf of Gdańsk were reported in samples from sites P104 and BMPK10, which were characterised by high proportion of sandy fraction (Szymczak-Żyła et al., 2017). The highest PAH levels in the Norwegian fjords were found in deeper sediment layers at sites C and E. These sites are influenced by emissions from urbanized and earlier industrialized areas of Oslo. The high variability of PAH concentrations was reported in specific sediment layers at some stations; for example, at site E the concentration of $\Sigma 12$ PAHs varied from 530 ng/g in uppermost layer (0–1 cm) to 4580 ng/g in 15–20 cm layer.

The stations studied differed not only in the concentration level but also in PAH composition patterns. The highest variation was found for 6-ring PAHs, and mean percentages ranged between 14.6% (BMPK10) and 38.6% (C). On a basis of cluster analysis applied to PAH profiles in sediment cores two groups of stations could be distinguished at a relative distance of ~75% (Fig. 3), but this classification is poorly significant since one of the clusters is very heterogeneous. At a distance of ~35%

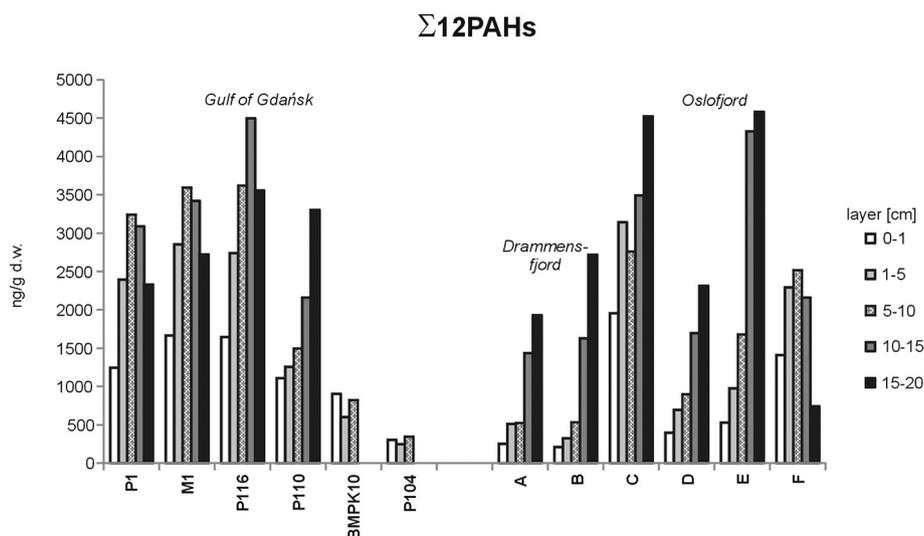


Fig. 2. Concentrations of $\Sigma 12$ PAHs in recent sediments in the Gulf of Gdańsk and Oslofjord/Drammensfjord [ng/g d.w.].

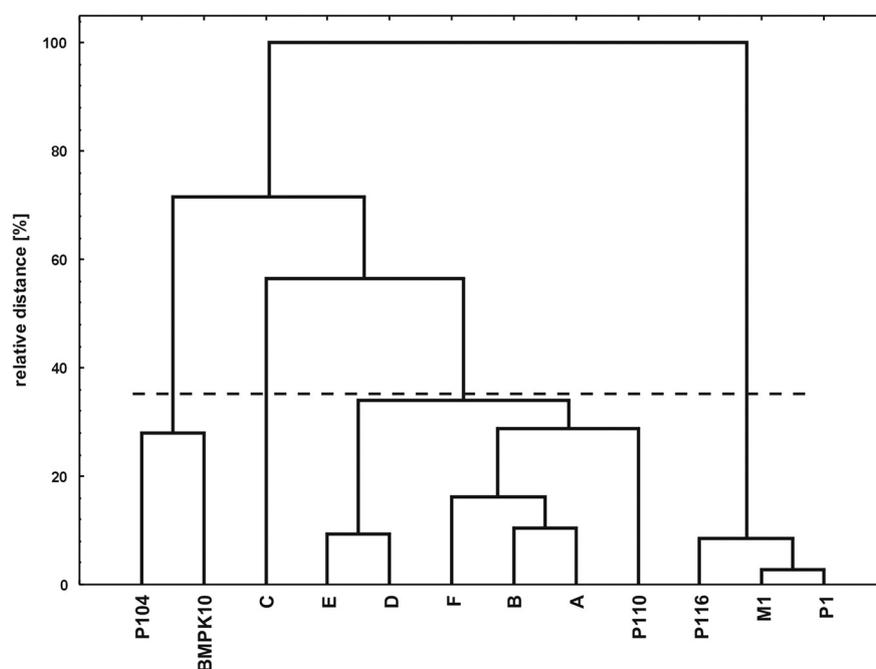


Fig. 3. Hierarchical dendrogram (cluster analysis - Ward's method, Euclidean distance) of stations from the Gulf of Gdańsk and Oslofjord/Drammensfjord based on percentages of parent PAHs in $\Sigma 12$ PAHs in sediment cores.

quite a homogenous cluster involving sites from the Norwegian fjords except site C can be identified. The PAH profiles in sediments from site C differ from those recorded at other Norwegian fjord stations, what may partly result from the specific location of this site in the southern part of the inner Oslofjord with enhanced exposure to shipping emissions. Besides, site C was the only fjord station, where good oxygen conditions in near-bottom water were recorded during the sampling campaign. Stations from the Gulf of Gdańsk belong to three clusters. The significant heterogeneity of these stations may reflect not only the distance from the coastline but also different environmental conditions (e.g. oxygen levels in bottom waters, grain-size composition of sediments, etc.) (Table 1) which strongly influence the fate of contaminants.

PAHs present in the environment are complex multicomponent mixtures that may originate from both natural and anthropogenic sources (Baumard et al., 1998). Most PAHs present in the environment are linked to human activities, and they are derived mainly from incomplete combustion of organic matter (pyrogenic) or spills of crude oil and its refined products (petrogenic) (Page et al., 1999). The ratios of concentrations of specific individual PAH compounds are commonly used to identify their dominant origin in environmental matrices (Lubecki and Kowalewska, 2012a). However, these molecular indices should be used with caution as the relative proportions of PAHs, especially low molecular vs. high molecular weight PAHs, may be strongly modified under environmental conditions (Wakeham, 1996). The fate of PAHs is not only influenced by abiotic processes (e.g. phototransformation) and biotic factors, but is also source dependant since PAHs of pyrogenic origin tend to be more resistant to biodegradation compared to petrogenic PAHs (Pereira et al., 1999). PAHs encapsulated within a particle, rather than adsorbed on the surface, may provide a PAH fingerprint which can survive over geological time scales (Yunker et al., 2002a). It should be born in mind that quantitative extraction of PAHs from soot is difficult because the compounds are extremely tightly bound to the sorbent matrix (Jonker and Koelmans, 2002a).

Several molecular indices were used in this study to assess the prevalent PAH sources (Table 2) and these indices suggest that PAHs in sediments from the Gulf of Gdańsk and Oslofjord/Drammensfjord are mainly of pyrogenic origin. The ratio of two dimethylphenanthrenes (1,7-dMPhen/(1,7- + 2,6-dMPhen)) indicates that these compounds may derive from mixed sources, i.e. from both coal combustion and

vehicle emissions. The ratio of Fla/(Fla + Py) also provides insight into the combustion source. For the Gulf of Gdańsk sediments, the Fla/(Fla + Py) ratio varied from 0.53 to 0.57, indicating combustion of biomass and coal as a major source of PAHs. Similar results were reported by Lubecki and Kowalewska (2012a) for recent sediments sampled between 2003 and 2007. Although the Fla/(Fla + Py) ratio in Norwegian fjord sediments fell within a range of 0.22–0.50, which is characteristic of liquid fossil fuel combustion and petrogenic input (Yunker et al., 2002b), pyrene can predominate over fluoranthene (Fla/(Fla + Py) < 0.5) in carbonaceous combustion residues (Fernandes and Brooks, 2003) and atmospheric urban particles (Benner et al., 1989). Oen et al. (2006) also reported Fla/(Fla + Py) < 0.5 for the clay and silt size fractions for sediments from Oslo and Drammen harbours. The analysis of IP/(IP + BPer) ratio indicates a higher contribution of PAHs originated from liquid fossil fuel combustion in fjord sediments, especially at site C, in comparison with the Gulf of Gdańsk.

3.2. Distribution of BC

Black carbon (BC) is considered as a marker for incomplete combustion of fossil fuels and biomass (Gustafsson and Gschwend, 1998). BC is one of the important factors that influence the fate of PAHs in sediments. As a strong geosorbent for hydrophobic contaminants, BC reduces the risk of remobilization of PAHs from sediments and subsequently their bioavailability to organisms (Cornelissen et al., 2005). The BC concentrations in sediment cores from the Gulf of Gdańsk and Oslofjord/Drammensfjord are presented in Table 1. BC contents in the sediments studied varied from below detection limit to 0.88%. BC levels were generally higher in the Gulf of Gdańsk (mean: 0.39%) than in Norwegian fjords (mean: 0.19%) and the difference between mean values for these areas was statistically significant (Mann–Whitney *U* test, $p < 0.05$). The highest BC concentrations (>0.8%) were found in the top 0–1 cm layers at sites P1, M1, P116; however, these elevated values may partly result from possible charring these samples when using CTO-375 method, as they contained relatively high contents of total nitrogen (~1%) (Accardi-Dey, 2003). The fraction of BC made up ~1–15% of the total organic carbon (TOC) in specific sediment layers. The median BC levels were equal to ~7–8% of TOC in the Gulf of Gdańsk and Norwegian fjords, respectively; and fall within the range of

Table 2
Ratios of PAH concentrations in sediment cores in the Gulf of Gdańsk and Oslofjord/Drammensfjord.

| Station | LMW/HMW-PAHs | Ant/(Phen + Ant) | Fla/(Fla + Py) | BaA/(BaA + Chry) | IP/(IP + BPer) | ΣmMPhens/Phen | 1,7-/-(1,7- + 2,6-) dMPhen |
|---|-----------------|-------------------|------------------------------------|--------------------|------------------------------------|-----------------|----------------------------|
| <i>Gulf of Gdańsk</i> | | | | | | | |
| P1 | 0.34–0.45 | 0.20–0.28 | 0.53–0.55 | 0.51–0.58 | 0.52–0.54 | 0.50–0.65 | 0.57–0.65 |
| M1 | 0.29–0.43 | 0.20–0.34 | 0.54–0.55 | 0.52–0.59 | 0.52–0.54 | 0.39–0.67 | 0.56–0.60 |
| P116 | 0.36–0.46 | 0.20–0.33 | 0.54–0.56 | 0.51–0.57 | 0.52–0.53 | 0.47–0.81 | 0.55–0.61 |
| P110 | 0.47–0.64 | 0.18–0.26 | 0.56–0.57 | 0.48–0.56 | 0.52–0.53 | 0.48–0.82 | 0.57–0.61 |
| BMPK10 | 0.64–1.07 | 0.34–0.55 | 0.53–0.55 | 0.39–0.62 | 0.46–0.49 | 0.54–0.77 | 0.54–0.60 |
| P104 | 0.59–0.87 | 0.16–0.33 | 0.56–0.57 | 0.47–0.53 | 0.51–0.51 | 0.44–0.62 | 0.60–0.63 |
| <i>Oslofjord/Drammensfjord</i> | | | | | | | |
| A | 0.54–0.75 | 0.27–0.47 | 0.37–0.47 | 0.50–0.62 | 0.48–0.50 | 0.55–0.91 | 0.62–0.69 |
| B | 0.51–0.73 | 0.24–0.46 | 0.25–0.47 | 0.53–0.63 | 0.45–0.50 | 0.60–0.85 | 0.63–0.72 |
| C | 0.36–0.44 | 0.46–0.58 | 0.27–0.43 | 0.55–0.56 | 0.28–0.34 | 0.57–0.69 | 0.54–0.58 |
| D | 0.39–0.73 | 0.25–0.47 | 0.27–0.49 | 0.53–0.63 | 0.44–0.48 | 0.52–0.71 | 0.63–0.70 |
| E | 0.46–0.68 | 0.33–0.60 | 0.22–0.50 | 0.54–0.58 | 0.46–0.48 | 0.52–0.95 | 0.57–0.69 |
| F | 0.47–0.52 | 0.33–0.43 | 0.40–0.49 | 0.55–0.56 | 0.45–0.49 | 0.60–0.75 | 0.62–0.69 |
| Molecular indices of PAH origin – literature data | | | | | | | |
| Pyrogenic | <1 ^a | >0.1 ^b | >0.5 ^b | >0.35 ^b | >0.5 ^b | <1 ^c | <0.45 ^d |
| | | | Combustion of grass, wood and coal | | Combustion of grass, wood and coal | | Vehicle emission |
| | | | 0.4–0.5 ^b | | 0.2–0.5 ^b | | 0.7–0.9 ^d |
| | | | Liquid fossil fuel combustion | | Liquid fossil fuel combustion | | Wood combustion |
| Petrogenic | >1 ^a | <0.1 ^b | <0.4 ^b | <0.2 ^b | <0.2 ^b | >2 ^c | – |

Abbreviations: LMW/HMW – low/high molecular weight; Ant – anthracene; Phen – phenanthrene; Fla. – fluoranthene; Py – pyrene; BaA – benzo(a)anthracene; Chry – chrysene; IP – indeno(1,2,3-cd)pyrene; BPer – benzo(ghi)perylene; ΣmMPhens – sum of monomethylphenanthrenes; 1,7/2,6-dMPhen – 1,7/2,6-dimethylphenanthrene.

^a Witt (2002).

^b Yunker et al. (2002b).

^c Zakaria et al. (2002).

^d Yunker et al. (2002a).

comparable values (range: 1–20%, median: 9%) for sediments from around the world (Cornelissen et al., 2005).

3.3. Correlation of PAHs with BC and TOC

BC is considered as a strong sorbent for PAHs, but literature data on the PAHs–BC relationship are inconsistent. Some authors reported strong positive correlations between PAHs and BC (e.g. Tsapakis et al., 2003; Oen et al., 2006; Feng et al., 2016), while others observed no such relationship (e.g. Kang et al., 2009; Honkonen and Rantalainen, 2013; Heath et al., 2006). The linear regression models were developed for all studied sediment samples (n = 56) to check if BC and TOC could be good predictors for distribution of PAHs in sediments. The major parameters of obtained models are presented in Table 3. Analysis of coefficients of determination shows that there was poor relationship between contents of Σ12PAHs and both BC (R² = 0.11) and TOC (R² = 0.18), what implies that only a small proportion of the variance of Σ12PAHs is predictable from BC (11%) and TOC (18%). The lack of strong correlation between concentrations of PAHs and BC seems to be unexpected since PAHs found in the sediments are derived mainly from

combustion processes and therefore should have the same source as BC. BC is considered to have especially stronger sorptive capabilities with respect to planar compounds like PAHs than non-BC organic matter (e.g. humic substances) (Cornelissen et al., 2005) and thus we may expect a higher correlation of PAHs with BC than with TOC. This discrepancy may partly result from the limitations of the CTO-375 method related to possible charring of organic matter and/or not equal detection of various types of pyrogenic matter (Marques et al., 2015; Nam et al., 2008). Different types of BC (e.g. diesel soot, coal soot, wood charcoal etc.), that may be present in sedimentary matrices, differ with respect to physicochemical parameters and may exhibit different sorption characteristics and non-linear isotherms for PAHs (Bucheli et al., 2004). In addition, BC was measured by mass, but adsorption of pollutants on BC particles depends mainly on their surface area (Agarwal and Bucheli, 2011). It is worth noting that some portion of PAHs may have been trapped in the soot core as a result of the soot formation process, therefore being unavailable for partitioning (Jonker and Koelmans, 2002b). The lack of relationship between PAHs and BC may also result from the restriction of sorption of PAHs by possible blocking pores in BC particles by amorphous non-pyrogenic organic matter or other

Table 3
Parameters of linear regression models for sediment cores from the Gulf of Gdańsk and Oslofjord/Drammensfjord.

| PAHs vs. BC | PAHs vs. BC | | | | PAHs vs. TOC | | | | |
|--------------------|-------------|-----------------------------|----------------|--------|--------------------|-----------------------------|----------------|-------|--------|
| | Slope | Standard error of the slope | R ² | p | Slope | Standard error of the slope | R ² | p | |
| Σ12PAHs | 2161.0 | 844.8 | 0.11* | 0.0134 | Σ12PAHs | 276.9 | 79.2 | 0.18* | 0.0009 |
| Σ3-ring PAHs | 152.1 | 59.5 | 0.11* | 0.0134 | Σ3-ring PAHs | 20.6 | 5.5 | 0.21* | 0.0004 |
| Σ4-ring PAHs | 476.1 | 269.2 | 0.05 | 0.0825 | Σ4-ring PAHs | 70.4 | 25.4 | 0.12* | 0.0076 |
| Σ5-ring PAHs | 789.6 | 257.3 | 0.15* | 0.0034 | Σ5-ring PAHs | 100.7 | 23.6 | 0.25* | 0.0001 |
| Σ6-ring PAHs | 743.2 | 295.5 | 0.10* | 0.0149 | Σ6-ring PAHs | 85.2 | 28.3 | 0.14* | 0.0040 |
| Σ(3 + 4)-ring PAHs | 628.2 | 322.6 | 0.07 | 0.0567 | Σ(3 + 4)-ring PAHs | 91.0 | 30.3 | 0.14* | 0.0040 |
| Σ(5 + 6)-ring PAHs | 1532.8 | 537.3 | 0.13* | 0.0061 | Σ(5 + 6)-ring PAHs | 185.9 | 50.5 | 0.20* | 0.0005 |
| ΣmMPhens | 83.2 | 19.2 | 0.26* | 0.0001 | ΣmMPhens | 10.4 | 1.7 | 0.42* | 0.0000 |
| ΣdMPhens | 112.0 | 20.5 | 0.36* | 0.0000 | ΣdMPhens | 13.3 | 1.7 | 0.52* | 0.0000 |

Abbreviations: BC – black carbon, TOC – total organic carbon, mMPhens – monomethylphenanthrenes, dMPhens – dimethylphenanthrenes.

* Statistically significant at p < 0.05.

molecules that compete for sorption sites at the BC surface (Pignatello et al., 2006).

Furthermore, higher correlations were observed for all groups of PAHs with TOC compared to BC (Table 3). The correlation between the levels of methylated phenanthrenes and BC as well as TOC appeared to be considerably stronger than in the case of the parent compounds (unsubstituted PAHs).

The correlations between the levels of $\Sigma 12$ PAHs and BC were comparable for the Gulf of Gdańsk ($R^2 = 0.13$) and Norwegian fjords ($R^2 = 0.12$), although linear regression slopes differed considerably (Supplementary information, Fig. S3.1a). However, if we exclude three samples containing the highest BC contents due to possible charring (0–1 cm layer; stations P1, M1, P116), the correlation of $\Sigma 12$ PAHs with BC increases ($R^2 = 0.58$) for the Gulf of Gdańsk. In the case of correlating $\Sigma 12$ PAHs to TOC, the differences in slopes were not so distinct between the two studied areas, but a higher coefficient of determination was reported for the Gulf of Gdańsk (Supplementary information, Fig. S3.1b).

3.4. Historical changes in energy and transport structure in Poland and Norway – background

3.4.1. Poland

Hard coal started being used in Poland in the 18th century, however, wood was still used as a basic energy resource until the middle of the 19th century (PMCWEC, 2014). Nowadays, these solid fuels are still the most frequently energy commodities in heating of households. Hard coal and wood fuel dominate in domestic furnaces, while district heating systems are mainly coal-fired. In 2011, hard coal used in Polish households accounted for 74% of its total consumption in the EU household sector (CSO, 2014).

In the second half of the 19th century crude oil started being used as an energy source and the first gas plants producing coke-oven gas were built (PMCWEC, 2014). After 1945 the energy sector in Poland became predominantly based on coal as very large coal-fired power plants were built at this time (Igliński et al., 2015). Nowadays coal is still of great importance to the Polish economy since it is the main source of both electrical and thermal energy used in Polish industry. Hard coal and brown coal (lignite) constituted 61% and 18% in the carriers' structure of primary energy production in 2013, respectively (Manowska et al., 2017), and they accounted for 98.7% in the Polish electricity fuel mix in 2005 (Chalvatzis and Hooper, 2009). The total current consumption of hard coal in Poland amounts to 70–80 million tons annually (CSO, 2016).

With regard to the transportation sector, the number of passenger cars has increased dramatically from 479 thousand in 1970 to over 20.7 million in 2015, and in the same period the number of lorries have also increased from 274 thousand to 3.1 million (CSO, 2017; Sobolewski, 1994). Between 1990 and 2015 consumption of diesel oil rose from 5.3 to 12 million tons, while consumption of gasoline increased from 3.8 million tons in 1990 to over 5 million tons in next years, but from 2000 a decreasing trend can be observed (CSO, 2005, 2016). It is worth noting that during the period 2002–2012 the fuel structure of cars used by households changed considerably in favour of LPG (liquefied petroleum gas) and diesel cars. The vast majority of diesel oil was used by trucks and in agriculture.

3.4.2. Norway

Wood has been a central source of energy in Norway since early times with the oldest stoves dating back to the 1300s (Haaland and Prøven, 2000). The source of fuel for cast iron stoves remained wood until the early 1900s when it became more usual to use coal and coke. The use of coal and coke as fuel remained the main source of heat for Norwegian households until the 1950s, even though building infrastructure for electricity had already begun in the largest cities in the mid-1800s (Bøeng, 2005). Bøeng and Holstad (2013) report that in

the 1960–1970s, 40% of energy use in Norwegian households was provided by paraffin, coal, coke as well as peat.

Municipal gas plants in Oslo and Drammen were in operation from about 1850 to 1970s (Christiania Gasværk in Oslo (1848–1978), Drammen Gasverk (1857–1959)). Initially these plants provided electricity for industry; however, service to households began to be available in the period 1910–1920 (Bøeng, 2005). Power stations were also being built with the first steam-electric power stations in operation in the late 1800s (Bøeng and Holstad, 2013). As demands for electricity increased, hydroelectric power replaced steam-electric power with intense construction of hydroelectric plants from 1974 until 1989 and currently electricity production is in Norway mainly based on hydro-power (Bøeng and Holstad, 2013).

The use of private cars started to dominate over rail transport by the late 1950s and their use increased further after import restrictions were removed in the 1960s (NOS, 1995). From the period 1960 to 1992, the number of passenger-kilometres for domestic passengers using private cars increased from 5 billion to about 40 billion passenger-kilometres (NOS, 1995). Energy needed for transportation has steadily increased relative to Norway's total energy usage (25% in 2006) as a result of an increase in road transportation. Both gasoline and diesel oil have been used as fuel for vehicles and 2006 marked the first year that sales of diesel oil were greater than gasoline (Wiik Toutain et al., 2008).

3.5. Anthropogenic emission history based on sedimentary records

3.5.1. Stations P1 and P116 (Gulf of Gdańsk)

The highest $\Sigma 12$ PAHs concentrations in the dated sediment core from site P1 were found in layers which were deposited between 1920s and early 1980s (Fig. 4). The sediment layers from station P116 had generally higher concentrations of PAHs compared to site P1, and the maximum PAH concentrations were reported for the period 1900s–1940s. The mean annual deposition $\Sigma 12$ PAHs fluxes in individual sediment layers were up to 112 ng/cm²/yr at site P116, which were higher than at site P1. As previously mentioned, the molecular markers of PAH origin indicated that PAHs at sites P1 and P116 have originated primarily from biomass and coal combustion processes (Table 2). The values of some diagnostic PAH ratios (i.e. Fla/(Fla + Py), IP/(IP + BPer)) were very similar in all sediment layers from these stations. The sediment cores, except uppermost layer (0–1 cm), were also homogenous in terms of BC concentrations (P1: 0.40–0.52%; P116: 0.45–0.54%), what may imply that accumulation rate of pyrogenic matter was rather steady. Analysis of $\Sigma 12$ PAHs distribution in the cores from the Gdańsk Deep suggests that the input of PAHs over the last 100 years was not subject to very high variation. Similar patterns were also reported for other areas of the Baltic Sea. The top sediment layers (up to 17/20 cm) from the Arkona Basin and Eastern Gotland Deep were characterised by homogenous and elevated PAH levels (Ricking and Schulz, 2002).

Although significant changes in energy structure, transportation, and other sectors occurred in Poland over the last 100 years, there were no very distinct changes in sedimentary PAH levels and composition patterns. This finding may be explained by the fact that the airborne PAHs in Poland have originated in the past mainly as a result of low-stack emissions from household heating based on coal and wood combustion (Adamczyk et al., 2017). Non-industrial combustion, mainly from households, accounted for ~86% (123,000 kg/yr) of total $\Sigma 4$ PAHs (BbF + BkF + BaP + IP) emissions in 2014, while emission from other sectors was distinctly lower (CSO, 2016). It is worth noting that the inputs of energy sector (0.2%) and road transport (1.8%) were estimated to be negligible in $\Sigma 4$ PAHs loadings. High loads of PAHs released through low-stack emissions from the household sector in Poland result mainly from (a) the preference for coal and wood due to relatively low cost of these energy sources, (b) the low efficiency of conversion in the furnaces and boilers, (c) a lack of equipment for reducing pollutant emission, (d) and long heating period (at least 5 months) (Adamczyk

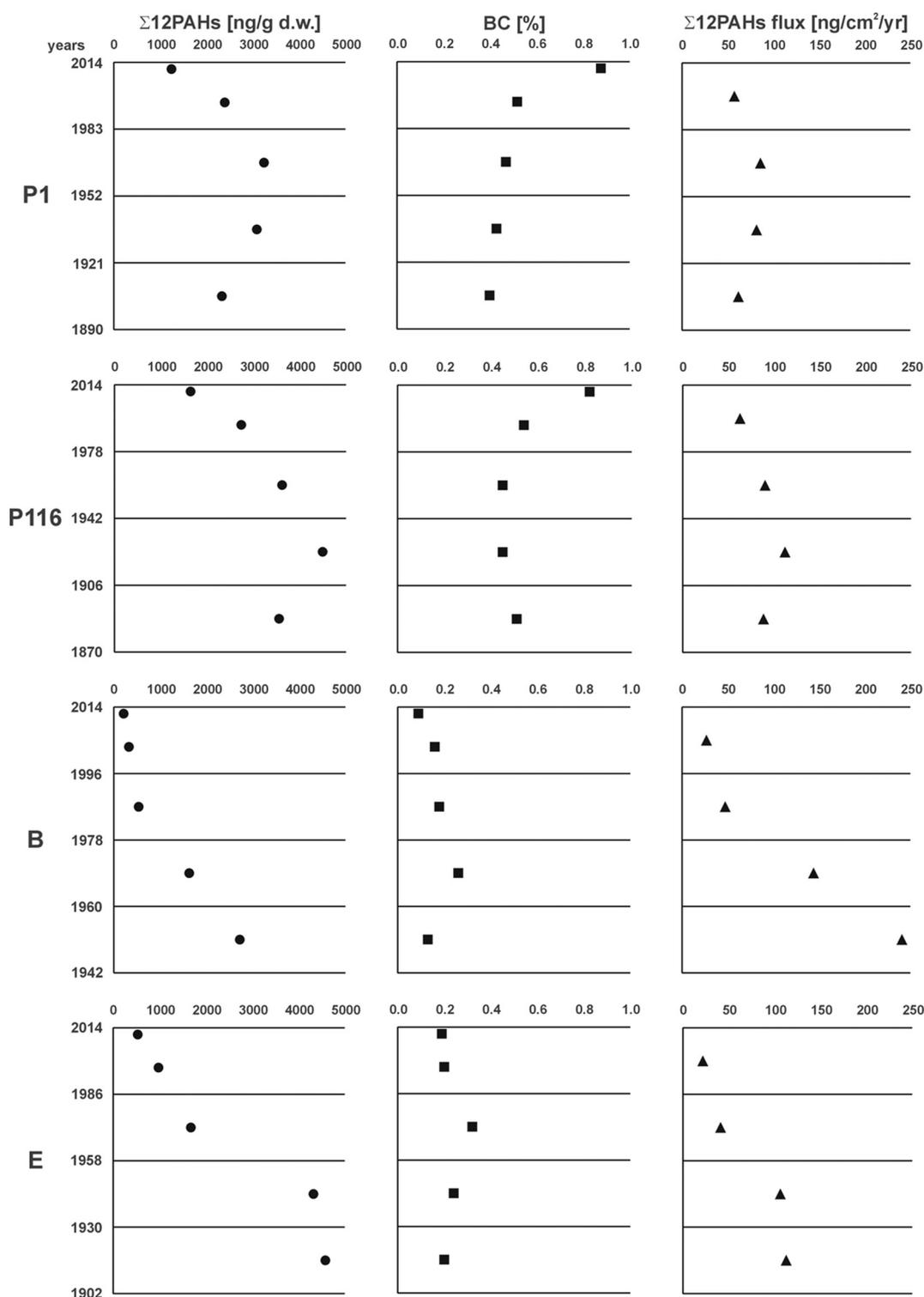


Fig. 4. Concentrations of $\Sigma 12\text{PAHs}$ and BC, and mean annual fluxes of $\Sigma 12\text{PAHs}$ in dated sediment cores from stations P1, P116 (Gulf of Gdańsk), B (Drammensfjord) and E (Oslofjord).

et al., 2017; Pyka and Wierchowski, 2016). The exceedances of target value for BaP ($>1 \text{ ng/m}^3$) have been reported in a significant number of locations in Poland for many years (CSO, 2016). Exposure to BaP is also significant and widespread in other countries in central and eastern Europe (EEA, 2016). It should be noted that distinctly higher BaP contents in PM₁₀ particles are generally reported in the heating season compared to the non-heating one. Similar temporal trends in airborne BaP concentrations were observed in the areas adjacent to the Gulf of Gdańsk, i.e. in the Gdańsk agglomeration (Lubecki and Kowalewska,

2012b) and in the province of Pomerania (northern Poland) (WIOŚ, 2016).

The challenges related to low-stack emissions in Poland have been aggravated by the lack of legal instruments related to the emission levels from small domestic heating sources (Adamczyk et al., 2017). However, the adoption of the 'anti-smog act' (Dz.U., 2015) in Poland as late as 2015, which is an amendment to the Environment Protection Law, may provoke local actions to decrease PAH loadings. It should be noted that slight decreases in the consumption of heating energy in

recent years have been reported mainly due to replacing some number of low-efficiency coal-fired boilers with more efficient devices, thermomodernisation and stricter construction standards (Stolarski et al., 2016).

3.5.2. Stations B (Drammensfjord) and E (Oslofjord)

The distinct rising trends of $\Sigma 12$ PAHs levels with sediment depth were observed for stations B and E, but there was no high variation in mass concentration of BC particles in these cores (Fig. 4). The dated stratified core from site B document temporal changes in pollutant concentrations since the early 1940s. The BC contents at station B were slightly elevated (0.26%) in the layer accumulated between 1960s and late 1970s. The highest PAH levels (~2700 ng/g) were reported for the period 1942–1960 followed by a distinct gradual decrease to ~200 ng/g in the uppermost sediment layer. The specific sediment layers at site B had lower PAH levels than those at site E, but annual inflow of PAHs to sediments was higher at station B. The temporal trends at both sites were very similar. The analysis of dated sediments from site E (Oslofjord) reflects the emission history back to the beginning of the 20th century (Fig. 4). The maximal PAH levels (~4300–~4600 ng/g) recorded in 10–20 cm section of sediment core from site E correspond to the period from ~1900 to ~1960, when coal and manufactured gas were the main energy sources in the Oslofjord (Arp et al., 2011), and coal and coke were still commonly used for heating of households (Bøeng, 2005).

The decline in PAH levels in upper sediment layers deposited in cores from stations B and E after ~1960 most likely reflects the rapid shift to hydropower and electric furnaces in this region of Norway. These findings are consistent with different periods of energy use that were mirrored in the studies of Arp et al. (2011). Similar PAH patterns were also reported by Cornelissen et al. (2008), who observed that PAH contents in sediments from Oslo harbour peaked between 1910 and 1950, after which mainly the transition from coal gasification to hydroelectric power entailed a strong decrease in PAH emissions. Decreasing trends in PAH levels at site E may also be due to the reductions in other urban discharges with the municipal waste water treatment plant built in 1963 and upgraded in subsequent years. PAHs did not vary with BC in the sediment core from site E. The BC levels peaked (0.32%) in the period between late 1950s and mid-1980s whereas the variability in other sediment sections was low (0.19–0.24%). Thus, the shift in dominant PAH sources after 1960 was not reflected in vertical distribution profiles of BC. The variation of the Fla/(Fla + Py) ratio along sediment cores (Table 2) suggests that not only quantitative but also qualitative changes in PAH loadings took place in the fjords studied.

In 2016, 43% of $\Sigma 4$ PAHs (BbF + BkF + BaP + IP) atmospheric emissions in Norway were derived from discharges related to the aluminium industry; however, the Oslofjord and border waters between Norway and Sweden have not been significantly influenced by emissions from aluminium industry (Næs and Oug, 1997). Although there was a reduction in total $\Sigma 4$ PAHs emissions in Norway between 1990 and 2016, emissions related to combustion processes from the transport sector increased from 800 to 1300 kg (Statistics Norway, 2017). In recent decades, declining trends in PAH loadings from households were observed especially after 2000, what may partly result from the fact that ovens made in late 1990s and later have significantly improved combustion and reduced pollutant emissions (Statistics Norway, 2016) as well as the municipality providing economic incentives for shifting from older to newer wood burning stoves (López-Aparicio et al., 2017).

In western Europe the decreasing trend in sedimentary PAH concentrations was generally observed after 1960s/1970s, similarly as in the Oslofjord/Drammensfjord. The reduced emissions of PAHs in western Europe were attributed to the replacement of coal by cleaner fuels (e.g. natural gas), improved combustion technologies and more effective emissions control (Leorri et al., 2014; Lorgeoux et al., 2016). In the region covering 31 member countries of European Environment Agency

emissions of PAHs decreased by 89% between 1990 and 2015, which resulted from a coupling of legislation with improved controls and abatement techniques (EEA, 2017). It is worth noting that PAH emissions in Denmark have increased by 33% since 1990 mainly due to the implementation of policy measures addressing climate change that have encouraged the burning of renewable materials (e.g. wood) in households.

Concentrations of BC, also reflect emissions sources. However, the temporal profiles of BC in the Gulf of Gdańsk and Oslofjord/Drammensfjord did not follow BC patterns in North America and Europe, where BC fluxes generally peaked between early 1900s and mid-1950s, and since 1960s declining trend was reported (Ruppel et al., 2015). Thus, the temporal patterns of mass concentrations of BC determined in this study did not provide new insights for historical reconstruction of changes in anthropogenic emissions.

4. Conclusions

This study illustrates that the distribution of PAHs deposited in sediments may differ significantly on a small spatial scale. The variation in sedimentary PAH levels in the Gulf of Gdańsk and the Oslofjord/Drammensfjord was generally comparable, with distinct local variations between some stations. PAHs of pyrogenic origin prevailed in both areas. Although pyrogenic PAHs may be transported over long distances, a combination of PAH inputs from local/regional sources and site specific conditions has a major influence on the distribution of PAHs in these marine coastal basins adjacent to areas impacted by anthropogenic pressure. In both the Gulf of Gdańsk and Oslofjord/Drammensfjord a weak correlation between concentrations of PAHs and BC in sediments was found.

Historical profiles of PAH concentrations in dated and well-laminated sediment cores suggest significant differences in temporal trends of anthropogenic emissions in the Gulf of Gdańsk and Norwegian fjords. The evolution in energy structure was especially evident in the Oslofjord, where transition from fossil fuel combustion to hydropower coincided with a sharp decline in sedimentary PAHs. In the Gulf of Gdańsk there was not so distinct temporal variation in PAH concentrations over the last 100 years despite significant changes in economic development. This discrepancy may be related to the overwhelming PAH inputs in Poland from burning solid fuels (coal, wood) for domestic heating purposes. The implementation of legislation and other activities addressed to restrict the use of solid fuels in residential heating should reduce PAH emissions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.07.300>.

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