

**Hydrocarbons in the sediments offshore of the Curonian Spit
(the south-eastern part of the Baltic Sea)*****Inna Nemirovskaya, Marina Ulyanova, Vadim Sivkov***

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Abstract Data regarding the content and composition of the hydrocarbons (HC) — aliphatic hydrocarbons (AHCs) and polycyclic aromatic hydrocarbons (PAHs) — are presented in comparison with the content of the total organic carbon (C_{org}) in the bottom sediments in the coastal area of the eastern part of the Gdansk Basin (Russian sector of the Baltic Sea). The HC and PAH distribution in the sediments confirm the dependence of hazardous substance accumulation on the organic carbon content and the sediment grain size of the affected sediment. Bigger concentrations of PAHs were also observed near the Pionersky port. Particular attention was paid to the PAHs content.

Keywords • hydrocarbons (aliphatic, polycyclic aromatic) • bottom sediments • total organic carbon

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INTRODUCTION

The Baltic Sea is considered to be one of the worst polluted marine areas in the world (HELCOM 2003). The sources of oil pollution in the Baltic Sea are primarily shipping, high urbanisation of the coast, and the development of industry in the coastal zone, including offshore oil field operation. Limited water exchange with the ocean, a relatively low water temperature, the prevalence of shallow depths (average 60 m), and the sudden changes in salinity increase the sensitivity of the Baltic Sea ecosystem to anthropogenic influences. According to experts, despite strong environmental protection measures and the reduced number of accidents, the overall environmental situation in the Baltic Sea in recent years remains an issue (Baltic Marine ... 2009; Risks of oil... 2013). One of the most sensitive and vulnerable regions in the south-eastern part of the Baltic Sea is an area offshore the Curonian Spit — a Russian-Lithuanian natural-cultural unit of UNESCO World Heritage.

The importance of protecting the Baltic Sea has been recognised since the 1970s in the form of the Helsinki Convention. Undoubtedly, a high level of environmental pollution by hydrocarbons is dangerous for the ecosystem. Thus, among others, certain polycyclic aromatic hydrocarbons (PAHs) are included to the list of priority hazardous substances under the Water Framework Directive, the Directive on Environmental Quality Standards (Directive 2008/105/EC). PAHs in the environment are widespread and have mutagenic, carcinogenic, and teratogenic effects (Freitag *et al.* 1985). PAHs may originate from both organic matter diagenesis and man-made processes (Simoneit 1977; LaFlamme, Hites 1978). Anthropogenic contributions to PAHs primarily outweigh contributions from natural sources (Hites *et al.* 1977).

There are several sources of possible hydrocarbons (HCs) pollution the area offshore of the Curonian Spit — the Kravtsovskoye offshore oilfield D-6 in the Kaliningrad region (Russia) and the Klaipėda oil terminal (Lithuania) that belongs to the large oil import/export

enterprise in the Baltic Sea region (Depellegrin *et al.* 2010). In the marine environment, hydrocarbons in the water phase tend to bind to particulate matter in amounts that depend on the properties of the PAHs and subsequently settle to the bottom sediment (Neff 1979). Accordingly, sediments are considered an important source of PAHs, especially for bottom fauna.

To determine the background conditions of HCs for the oil pollution of the south-eastern part of the Baltic Sea, especially in the area adjacent to the Curonian Spit, the aliphatic hydrocarbons (AHCs) and PAHs were examined in the bottom sediments. The study was performed within the NATO Science for Peace programme project “Development of solutions for effective oil spill management in the South-Eastern Baltic” (SfP984359) and the Kravtsovskoye oilfield monitoring programme.

MATERIAL AND METHODS

Surface (0–5 cm) bottom sediments were collected during the summer period of 2012 to 2013 in the offshore coastal area of the Kaliningrad region (points 1, 3–9) (Fig. 1). In addition, samples were collected in a deep part of the Gdansk Basin (point 22) and near the oil platform D-6 (point 9L, Kravtsovskoye oilfield). All the samples were collected using measures to prevent contamination.

The concentration of HCs was determined via infrared

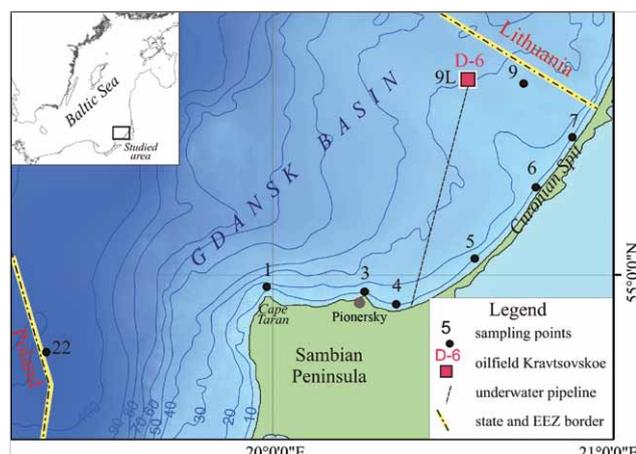


Fig. 1 Sampling points location combined with bathymetry. Compiled by I. Nemirovskaya, 2014.

spectroscopy according to the 2930 cm^{-1} strip in an equivalent of Simard’s mixture (37.5 % isooctane, 37.5 % hexadecane, and 25 % benzene) using an IR Affinity-1 Shimadzu instrument (Japan). This method is used as a referee method when analysing petroleum HCs (Guidelines ..., 1996). A factor of 0.86 was used to translate the AHCs concentrations into the C_{org} concentrations (Nemirovskaya 2013). The composition of the alkanes was determined via capillary gas chromatography (a 30 m long column, liquid phase ZB-5) using an Intersmat GC 121-2 chromatograph

equipped with a flame ionisation detector with the temperature programmed to be within the range of 100 to 320 $^{\circ}\text{C}$ at a rate of 8 $^{\circ}\text{C}/\text{min}$.

The content and composition of the PAHs were determined via high-performance liquid chromatography using a *LC-20 Prominence* (Shimadzu). A mixture of acetonitrile with water under gradient conditions (50 to 90 % acetonitrile) was used as the eluent; the apparatus was equipped with a fluorescent detector *RF-20A* with programmable wavelengths of absorption and excitation. The calculations were performed using the LC Solution software. The equipment was standardised with the individual PAHs, and their mixtures were manufactured by Supelco Co. As a result, 16 key polyarenes recommended for studying the pollution of marine objects by the Environmental Protection Agency (USA) were identified.

The organic carbon in the sediment samples was determined via dry combustion using an AH 7529 analyser (Lyutsarev 1986). A filter or its fragment was placed into a porcelain crucible; next, the common procedures for determining C_{org} in bottom sediments were used. The sensitivity of the apparatus was 6 $\mu\text{g}/\text{g}$ of carbon in a sample at a precision of 3 to 6 relative %.

RESULTS

Most of the sediment samples were composed by sand (points 3, 5, 6, 7, and 9) and gravelly sand (points 1, 4, and 9L). Point 22 was located in the area of clayey mud (Emelyanov 2001) and was considered for comparison between the shallow sandy and the deep aleuropelitic areas (Table 1). Types of bottom sediments are classified according to Bezrukov, Lisitzin (1960).

Table 1 Hydrocarbon concentration and organic carbon content in the surface sediments of the south-eastern part of the Baltic Sea (Russian sector) measured in 2012 and 2013. Compiled by I. Nemirovskaya, 2014.

Point	Sediment type	AHC concentration, $\mu\text{g}/\text{g}$		C_{org} content, %	
		2012	2013	2012	2013
1	Gravelly sand	-	15.74	-	0.432
3	Sand	6.25	6.17	0	0.024
4	Gravelly sand	15.50	4.12	0.877	0.020
5	Sand	4.81	4.53	0.013	0.017
6	Sand	5.25	4.45	0.006	0.023
7	Sand	3.63	3.78	0	0.046
9	Sand	4.59	3.71	0.005	0.008
22	Clayey mud	75.60	39.71	4.100	4.224
9L	Gravelly sand	8.53	3.50	0	0.001

The contents of organic compounds is normally higher in the silty sediments (particularly in the case of the dominant fraction being < 0.1 mm) than in the coarsely dispersed sediments. The clayey mud in the deeper part (point 22) was characterised by a high C_{org} content (4.1–4.2 %). The organic carbon content in the bottom sediments of the shallow part varied within the ranges of 0.0001–0.88 % measured in 2012 and 0.008–0.43 % measured in 2013, with the average value for the two years of 0.11 % (Table 1). The maximum C_{org} content was measured in 2012 near the Curonian Spit root (0.88 % at point 4); in 2013, this value was reached offshore of the Cape Taran area (0.43 % at point 1). Minimal contents were measured at points 2 and 7 (measured in 2012) and at point 9 (measured in 2013).

The highest HC concentrations were detected in the clayey mud at point 22 (40–76 $\mu\text{g/g}$, Table 1, Fig. 2), and the lowest HC concentrations were revealed at the sands of point 7 (3.6–3.8 $\mu\text{g/g}$). In the coastal area, the HC concentrations were similar, and varied within the ranges of 3.6–15.5 $\mu\text{g/g}$ and 3.5 to 15.7 $\mu\text{g/g}$, respectively. More HC contamination was revealed in the bottom sediments in the area of Pionersky Port (6.2–15.5 $\mu\text{g/g}$ at points 3 and 4). Measurements carried out in 2013 have shown that Cape Taran area (15.7 $\mu\text{g/g}$) and the Pionersky Port (6.2 $\mu\text{g/g}$) were contaminated the most. The HC concentration values measured in 2012 and 2013 in the sediments along the Curonian Spit varied from 3.6 to 5.25 $\mu\text{g/g}$ and from 3.7 to 4.5 $\mu\text{g/g}$ respectively. In the summer of 2013, sandy sediments in the area near platform D-6 were less HC contaminated in comparison with situation identified in 2009–2012.

The proportion of HCs in the C_{org} in the sands of the coastal area was up to 2.3 % (measured in 2012) and 7.9 % (measured in 2013) (Fig. 2); in comparison, this value for the clayey mud of the Gdansk Deep (point 22) was 0.08 % and 0.16 %. The highest proportion of HCs in the C_{org} (30 %) was revealed for the light brown fine grained sands with a large quantity of fine pebbles collected in the vicinity of platform D-6 (point 9L),

which means that the organic matter of the sediments at point 9L consisted almost exclusively of HCs.

At the background level, the concentrations of HCs do not normally exceed 10 $\mu\text{g/g}$ in the sands and are up to 100 $\mu\text{g/g}$ in the silty sediments (Galimov *et al.* 2006; Nemirovskaya 2013; Tolosa *et al.* 2004). The proportion of HCs in the C_{org} is normally $\leq 1\%$ (Nemirovskaya 2013). Within the examined area of the Gdansk Basin, the AHC concentrations at the majority of the points corresponded to a background level. The average content of HCs in the sandy sediments of the coastal zone for the studied period was 6.3 $\mu\text{g/g}$, and the proportion of HCs in the C_{org} was 2.8 % on average.

A positive correlation was revealed for the HC concentration in the sediment and the C_{org} content: $r(\text{HC}-C_{org}) = 0.99$ for 2012 results, and $r(\text{HC}-C_{org}) = 0.97$ for ones of 2013. A similar dependence was observed for different areas of the Baltic Sea (Witt, Matthäus 2001; Witt 2002). This observation may be an indication that the major part of the HCs are from natural sources, *i.e.*, phytoplankton and terrigenous compounds. In comparison, the concentration of total hydrocarbons in the Šventoji Port basin (Lithuania) exhibited only a mediocre relationship with the content of the total organics in the sediments (Stakėnienė *et al.* 2010). This result is an indication that the majority of the total hydrocarbons are represented by petroleum hydrocarbons.

The composition of alkanes of AHC at some points in the coastal area (points 3, 4, and 9L) was an adequate form of oil (Fig. 3). Markers also indicated the origin of the oil AHC because the values of CPI were < 1. In contrast, point 9L, where in 2008–2012, the genesis of the oil of AHC was established, was dominated by terrigenous allochthonous homolog's, as the value of CPI reached a value of 2.42. The intensity of the microbial processes exhibit maxima at $n\text{-C}_{19}$ and $n\text{-C}_{21}$, and increased the proportion of low molecular weight homologues in their composition: the ratio of

$$\frac{\sum C_{(12-24)}}{\sum C_{(25-35)}} > 1.$$

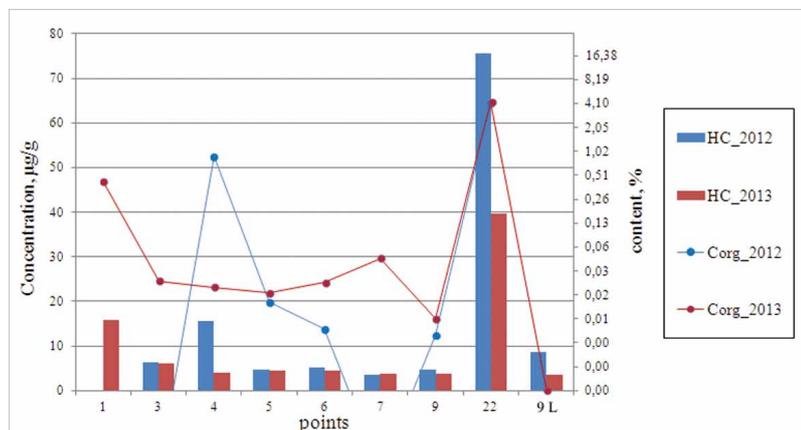


Fig. 2 Hydrocarbon concentration determined using the IR method in bottom sediments and the C_{org} content (logarithmic scale) in 2012–2013 in the south-eastern part of the Baltic Sea. Compiled by I. Nemirovskaya, 2014.

The contents of the PAHs in the bottom sediments in the coastal zone varied from 3 to 39 ng/g; in the deeper area (point 22), this value was 19 ng/g. A previous study presented similar results: 2.6–313 ng/g (in 2008), 0.3–16 ng/g (in 2010) and 4–57 ng/g (in 2011) (Nemirovskaya, Sivkov 2012).

DISCUSSION

Currently, there is a lack of published data on the PAH concentrations in the sediments of the eastern part of Gdansk Basin (Russian sector). Because PAHs are one of the most hazardous substances to

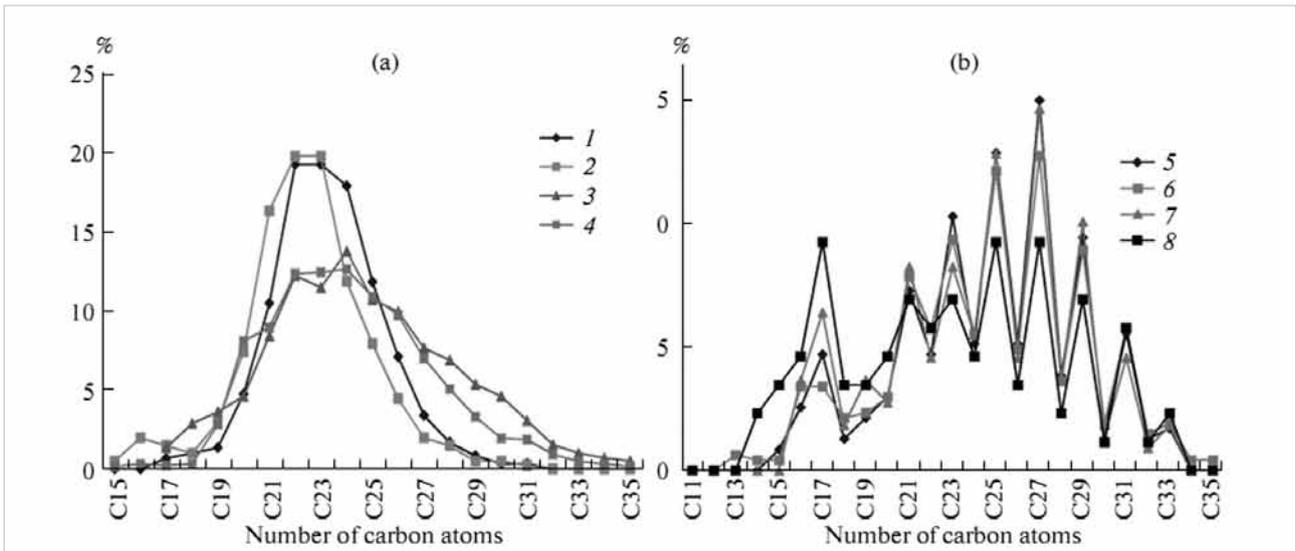


Fig. 3 The composition of alkanes of hydrocarbons in sediments sampled in summer 2013 (the location of the points is shown in Fig. 1). Compiled by I. Nemirovskaya, 2014.

the ecosystem, the data from 2008, 2010, 2011, and 2013 were combined and analysed not only for the coastal part but also for the entire eastern part of the Russian sector to provide a general representation of the PAH background level (Fig. 4). Bigger concentrations were revealed in the deepest part of the studied area. For the entire monitoring period, the PAH concentration was found to depend on the grain-size of the bottom sediments and on the anthropogenic compound. Note that no contamination by PAHs originated from oil platform D-6. The adjacent area to the Curonian Spit was characterised by lower PAH concentrations than that of the northern coast of the Sambian Peninsula. This result may be explained by the high level of industrial and domestic load coming with the river runoff from the densely populated Sambian Peninsula. Additionally, this area is characterised by a predominance of abrasion processes, whereas the anthropogenic activity is not so active at the Curonian Spit and its coastal zone corresponds to the transition accumulative sedimentary area (Sivkov *et al.* 2012).

According to the HELCOM Thematic Assessment of

Hazardous Substances (HELCOM 2010), the highest levels of PAHs are observed in lagoon areas, near harbours, or in the accumulation areas where the smaller or fine particulates have higher concentrations of

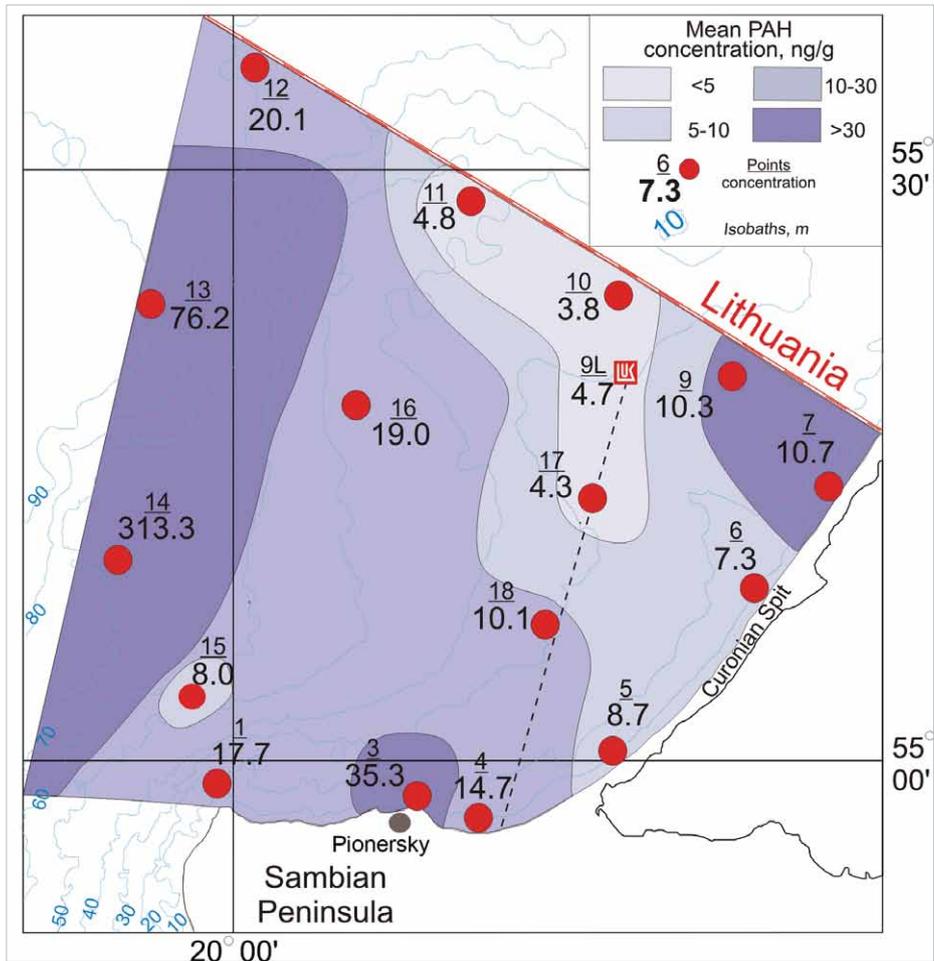


Fig. 4 Average PAH concentration distribution in the surface sediments of the eastern part of the Gdansk Basin (Russian sector) based on data from 2008 (Nemirovskaya *et al.* 2011), 2010, 2011 (Nemirovskaya, Sivkov 2012), and 2013. Compiled by I. Nemirovskaya, 2014.

PAHs than the larger or coarse particulates. One of the main pathways of the production of PAHs is the relatively rapid (days to years) transformation or diagenesis of organic matter as a part of the changes undergone by bi-molecules and related organic matter after the initial deposition in sediments (Boehm 2006). Likewise, in our study, high PAH concentrations were found in similar areas of the eastern part of the Gdansk Basin.

An average PAH concentration for the studied region for 2008 to 2013 was 18.3 ng/g. Considering that this PAHs monitoring period is one of the longest in the eastern part of the Gdansk Basin, it is possible to indicate the value of 18.3 ng/g as being a background value.

Compared with the other regions of the Baltic Sea, the contamination of the Russian sector of the eastern part of the Gdansk Basin by PAHs may be considered as insignificant. Thus, in the upper (0–20 cm) silt layer of the Mecklenburg Bay, the PAH concentration was 724 to 1697 ng/g, in the German coastal zone (silts mainly) the PAH concentration was 845 to 2180 ng/g (Witt, Trost 1999), in the fine-grained sands of the southern part of the Gulf of Gdansk, the PAH concentration was 300 to 500 ng/g, and offshore of the Klaipeda Strait, the PAH concentration was 100–200 ng/g (Bojakowska, Uscinowicz 2011).

PAHs are produced by natural and anthropogenic processes (Boehm 2006) and primarily come into the marine environment with the atmospheric aerosol fallout (AMAP 2007; NRC 2003). The types of PAH anthropogenic sources consist of crude oil emission (petrogenic source) (Bence *et al.* 1996) and all types of fossil fuel incomplete burning (pyrolytic sources) (Hites *et al.* 1977). Some PAHs are of natural origin, but the majority of PAHs are formed due to anthropogenic activity. Pyrolytic sources dominate in the PAH contamination of the sediments and biota of the Baltic Sea (Neff 2004). However, several investigations revealed significant petrogenic PAH concentrations in the Gulf of Finland and several areas in the western Baltic Sea. This result may indicate that the anthropogenic precipitation from marine transport is the main source of PAHs in these areas.

The dominant homologues comprising the PAH surface layer of sediments include naphthalene, fluoranthene, pyrene, phenanthrene, chrysene and perylene

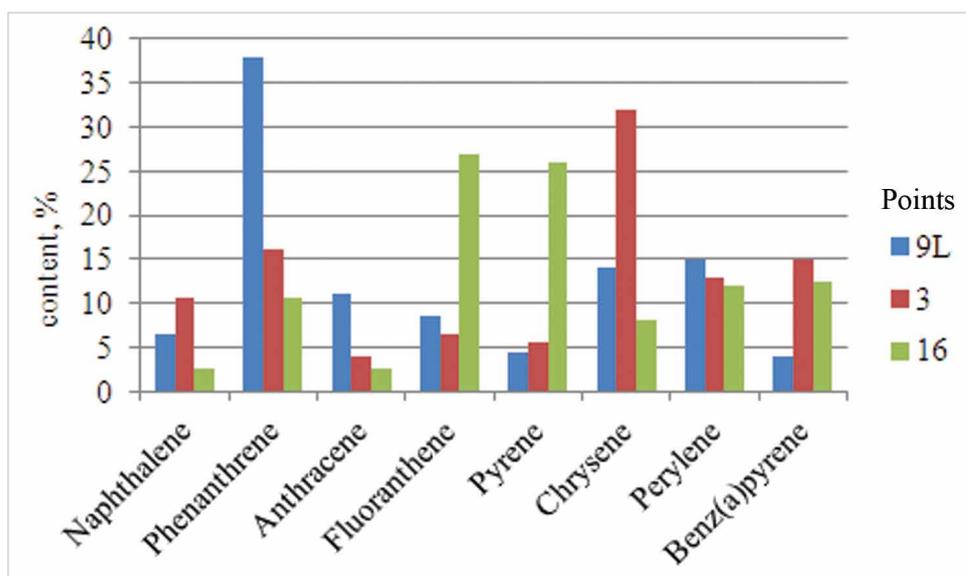


Fig. 5 The content and composition of the dominant PAHs in sediments measured in summer of 2013 (the location of the points are shown in Fig. 1). Compiled by I.Nemirovskaya, 2014.

(Fig. 5). The last three polyarenes belong to the PAHs of the geochemical background.

Oils consisting of PAHs increased in proportion with the amount of methylated naphthalene and its homologues (Tolosa *et al.* 2004). Relatively high concentrations of naphthalene (especially at point 3) may indicate the impact of oil. At the same point, the proportion of chrysene (up to 32 %) increased, which is a ubiquitous environmental contaminant that occurs as a product of the incomplete combustion of organic compounds. Among the other environmental anthropogenic sources of chrysene, diesel exhausts may explain the high content of this individual PAH in the sediments of the Pionersky Port area (point 3). Diesel exhausts may also explain the bigger benz(a)pyrene (15 %) content, but its concentration does not exceed 20 ng/g – the maximum permissible concentration (MPC) for benz(a)pyrene in soils. The minor part of the total PAHs consisted of benz(a)pyrene, which is the most carcinogenic among the polyarenes identified because its content in the products of burning is lower than that of pyrene and it is less stable (Rovinskii *et al.* 1988). A high content of phenanthrene in the area of the platform may originate from both petrogenic and pyrogenic sources and so are considered as being from a “mixed” source. In any case, phenanthrene is not classifiable as to its carcinogenicity to humans. Perylene forms in a sedimentary column which is rich in terrigenous plant material (Venkatesan, Kaplan 1987). The proportion of perylene of diagenetic origin is > 10% (Page *et al.* 1999; Tolosa *et al.* 2004).

In the bottom sediments near the D-6 oil platform, the average content of AHC consistently decreased (µg/g): 128 (2008) > 16 (2009) < 22 (2010) > 5 (2011) = 5 (2012) = 5 (2013). Consequently, there was a sharp decrease in the concentration from 2008 to 2009, followed by the content remaining approxima-

tely constant; also, it was lower than the background for sandy sediments. It is remarkable that in 2008, at point 9L, the AHC share (based on TOC) as part of the TOC reached 98 %, *i.e.*, the organic matter practically consisted of AHC (A review... 2008). On the contrary, in the summer of 2013, the relative content of AHC to the TOC was 3.4 %.

Despite the fact that the HCs near platform D-6 are predominantly of oil origin, it is quite difficult to determine the origin of the bottom sediments. In the marine environment, the HCs are rapidly transformed during sedimentation in the boundary layer between the water and the bottom and in the surface layer of the bottom sediments (Il'inskii, Semenenko 2001; Nemirovskaya 2013). In addition, it is possible that the HCs in this area seep from the sedimentary mass with fluid currents as zones of activation of geodynamic processes were detected there (Patin 2008), which promote HCs to enter into the sea. These seeps are concentrated in the areas where oil and gas basins are common and are confined to the water areas of oil fields, which account for no more than 10–15 % of the total size of the Global Ocean (Nemirovskaya 2013). The contribution of petrogenic HCs to the total quantity of HCs coming into the ocean is 600 ktpa, *i.e.*, 48 % of the total quantity coming into the ocean (NRC 2003). In particular, the daily inflow of HCs in a ~ 1.5 km long area in the Santa Barbara Channel (California) is estimated at 10 to 15 t per day (Natural oil seeps 2002). It is known that in waters where the flow of oil can occur from the bottom, the percolation rate varies in time and space (Patin 2008). Perhaps this phenomenon is related to the variability of the AHC concentrations in sediments in different years of the study. The oil seeps in the area are a source of energy that is recovered strongly and readily undergoes microbial oxidation. Therefore, in the areas where common fluid flows on the surface of precipitation, the development of oil-oxidising microorganisms occurs.

A composition of alkanes (just as in the vicinity of platform D-6) characterised by the occurrence of the homologs of the petroleum series was observed previously in the bottom sediments of the southeastern portion of the Baltic Sea within acoustically anomalous areas (Nemirovskaya 2013). The values of the CPI in the alkanes of the sediments varied from 1.03 to 1.06, with the maximum being within the range of $n\text{-C}_{24}\text{--C}_{27}$. Low molecular homologs accounted for only 0.1–1.1% of the sum of the alkanes, and there was almost no naphthene–aromatic “bump”. A similar composition of alkanes was observed at some points in the sedimentary mass at the 16 to 19 m depth, while the HCs in the surface layer (0–3 cm horizon) were represented by a transitional type of organic matter.

CONCLUSIONS

In bottom sediments of the eastern part of the Gdansk Basin (the Russian sector of the Baltic Sea), the content of the HCs depends on their grain size type. Therefore, higher concentrations were observed in the muddy sediments characterised by high dispersion and, consequently, the adsorption ability of the mud.

The concentrations of hydrocarbons and organic carbon in the bottom sediments in the coastal sandy area exhibit a strong direct relationship. The composition of the HCs is such that it is formed by natural sources, *i.e.*, phytoplankton and terrigenous compounds. It may be suggested that an increase of the petroleum HCs concentration (for example, in the case of emergency oil outflow) will provide a lower level of correlation between the HC and the C_{org} content in the sandy sediments.

The hydrocarbons concentration in the bottom sediments of the coastal area of the eastern part of the Gdansk Basin measured in 2012 to 2013 ranges from 3.5 µg/g to 15.7 µg/g. The maximal amounts of hydrocarbons are accumulated offshore of the northern coast of the Sambian Peninsula.

The distribution of HCs and PAHs in the sediments of the studied area coincides only generally. The geochemical relationships are not typical for the concentrations of these hydrocarbon classes. The local variations of biological and hydrodynamical conditions of the formation of organic matter as well as anthropogenic sources influence the quantity and composition distribution of the PAHs. Thus, the maximum average concentrations were confined to the deeper area of the Gdansk Basin (natural reasons) and to the Pionersky Port (anthropogenic factor).

Acknowledgments

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