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DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE SEA WATER COLUMN

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Abstract. The most intensive traffic in the world is going in the Baltic Sea. Consequences of intensive navigation are illegal or accidental oil spills. Following a spill, the soluble fraction of polycyclic aromatic hydrocarbons (PAH) is rapidly released into the water column. These remain dissolved in seawater over an extended period of time, even should the insoluble fraction be removed. Therefore, it is necessary to know how fast and what polycyclic aromatic hydrocarbons start releasing from the film of spilled oil. During an experiment, it was aimed to determine maximal concentrations of that. PAH were analysed in the dissolved and suspended phases in the water column. The study was undertaken under controlled conditions so as to minimize the variability of environmental factors such as temperature and hydrodynamics. After two weeks of the experiment, the following low-molecular weight hydrocarbons were detected: naphthalene (Naph), phenanthrene (Phe) and anthracene (Antr). No high-molecular weight hydrocarbons were detected within the total time of the experiment (8 weeks). The distributions of PAHs were measured in the dissolved and suspended phases, where total concentration of PAHs ranged from 19.01 ng L⁻¹ to 194.70 ng L⁻¹ in the dissolved phase and from 5.14 to 63.92 ng L⁻¹ in the suspended phase. The release of PAHs from the film started immediately after the spill reaching 194.70 ng L⁻¹ in the dissolved phase and 63.92 ng L⁻¹ in the suspended phase near the bottom of water column after 1 – 2 hours. In the dissolved phase, 2 – 3 ring PAHs dominated (60 – 80 %), whereas the highest amount of 4 – 6 ring PAHs (55 – 90 %) was found in the suspended phase.
Key words: oil spill, polycyclic aromatic hydrocarbons, distribution

1. Introduction

Oil spills are unavoidable and adverse consequence in production and transportation of oil and related refined products. During recent forty years, over two thirds of all large oil spills (> 700 tons) have happened in open and internal waters, and, though the number of cases of large and the average oil spills (7 – 700 tons) from vessels has significantly decreased, however, oil transportation by sea has been continuously increasing since the middle of nineties of 20th century [1]. About 90% of oil and its products are being transported by sea in Europe [2].

Anthropogenic sources, such as pyrolytic hydrocarbons (combustion of fossil fuel, waste and biomass, industrial processes, etc.) and petrogenic hydrocarbons (oil spills, ballast water discharges, oil reproduction, etc.) exceed amounts of sources of natural hydrocarbons (forest fires, etc.). Different ways of access of hydrocarbons into the water ecosystem have been estimated: (i) direct releases, e.g., oil spills and de-ballasting, coastal industrial emissions into water, (ii) continental release and urban and/or industrial waste existing in rivers, (iii) atmospheric deposition of gases and aerosols [3]. Accidents

related to spills of petroleum hydrocarbons happen in the world quite often and the annual oil spill in the sea exceeds 1300 kilos [4]. Spill of crude oil makes profoundly serious harm to the ocean and particularly to the coastal areas. It has been estimated that even such small concentrations of PAHs (0.4 ppb) in water may be harmful to eggs and larvae of the herring [5]. Most often, petroleum hydrocarbons are most harmful to the fish in their early period due to vulnerability of their tissue or enzyme inhibition, and the effect may be described as stress, genetic damage, slower growing and high mortality [6].

Crude oil contains [7] different types of polycyclic aromatic hydrocarbons, i.e., from two-aromatic-ring to compound complex four-five-ring ones. Environmental Agency (US-EPA, EEA-EU) has listed 16 polycyclic aromatic hydrocarbons (PAH) as priority pollutants due to their toxic, mutagenic and/or cancerogenic effect. Four-five-ring PAHs are assigned to high mutagenic and cancerogenic level and two-three-ring PAHs are less mutagenic, however, they are more toxic [8]. Crude oil from different extraction deposits can feature different distribution of PAHs in water. Moreover, majority of PAH compounds are more resistant to weathering than their saturated analogues (n-alkanes, isoprenoids) and volatile alkylbenzene compounds; therefore, PAHs are important in evaluation of oil spills. When researching distribution of PAHs, differences can be noticed even between products of the same class [9]. Polycyclic aromatic hydrocarbons (PAH) are a group of persistent organic pollutants (POP), which can migrate in big distances and remain in the environment for many years [10]. The route of exposure of PAH in the environment basically depends on the number of rings in the molecule and pH of environmental conditions, temperature, and salinity [11]. Distribution of PAHs in dissolved and particulate phases in the water-column affects assimilation of PAHs by water organisms. Dissolved PAHs are being transported due to molecular and turbulent diffusions and advection, and compounds of fractions are being transported due to turbulent diffusion and sedimentation, including subsidence and re-suspension [12]. Interaction of hydrophobic organic compounds with dissolved organic coal reduces vertical diffusion of hydrophobic compounds in the water-column and biological accessibility of hydrophobic compounds in the water ecosystems [13].

Mathematical modelling of oil spill is significant means purposed for research of evaluation of environmental effect. In mathematical models, the oil spill is being analysed as distribution of the solid oil or pseudo-components but not of individual hydrocarbons in the marine environment [14]. Different petroleum hydrocarbons behave differently in the marine environment; therefore, each hydrocarbon must bear its own algorithm to describe its modelled behaviour. Moreover, many scientific publications research diffusion of dispersed oil fractions into the water-column as the eddy diffusion that is described by turbulent energy equation [15] but not as the molecular diffusion of individual petroleum hydrocarbons. This difference between the molecular and fraction diffusion is important in order to find out exact concentrations of pollutants but not their average numbers; therefore, possibilities of models to define exact concentrations are limited. The molecular diffusion of petroleum hydrocarbons from the oil film into the water-column is significant process when researching mass transfer processes.

In real oil spill situations, it is rushed to liquidate the emergency and the actual effect of oil to the sea ecosystem is not known. The aim of the research was to determine what polycyclic aromatic hydrocarbons diverge initially from the film of spilled oil, how quickly they start diverging and what maximum concentrations can reach the sea bottom and/or accumulate in biota. The first two questions are important in order to execute efficiently operation of oil spill liquidation. The third question is important in order to estimate maximum damage to the sea ecosystem.

2. Method and Materials

2.1. Experiment

The experiment was carried out under laboratory conditions, while imitating the oil spill, in the polyvinylchloride cylinders. To carry out the research, experimental stand, consisting of 8 polyvinylchloride cylinders (height – 1.1 m, diameter – 0.2 m), was designed. The cylinders were modified using infusive systems for water sampling in three water layers, i.e., the surface, middle and demersal layers. The cylinders were sealed with a transparent methacrylate plate. The cylinders were

filled up with 34 L of the seawater (the Baltic Sea water, salinity – 6.2 PSU, static conditions). Four different environmental conditions were imitated in the cylinders: 2A – seawater, sand (static conditions, 14 °C), 4A – acidified seawater, sand (static conditions, 14 °C), 5A – seawater, sand (static conditions, 25 °C), 6A – acidified seawater, sand (static conditions, 25 °C). A sample of 50 g of the crude oil (Kretinga crude oil) was poured into the cylinders. The control cylinders (without crude oil) were prepared as well. The experimental set up was monitored over a period of 60 days. Sampling was made after 2, 4, 6 and 8 weeks. Samples were taken from 3 different water-column layers:

1. – the surface water layer under the film (~ 5 cm from the film of crude oil);
2. – the middle layer (~ 42 cm from the sand surface)
3. – the demersal water layer (~ 5 cm from the sand surface).

2.2. Chemical analysis

Samples of 50 ml were taken for research. The water samples were extracted 3 times with the mixture of 20 mL of hexane and dichloromethane (1:2) (Sigma Aldrich, CHROMASOLV®, for HPLC, ≥95 %). Collected extracts were fed through analytically pure anhydrous sodium sulphate (Sigma Aldrich, anhydrous, Redi-Dri™, ACS reagent, ≥99%). The extract was concentrated to nearly dry by rotary evaporation (IKA RV-10 Digital), then solvent-exchanged into hexane around 1 mL followed by a clean-up procedure. The extracts were cleaned up using a 5 mL in 2:3 (v/v) alumina (SIGMA-ALDRICH, Aluminium oxide, puriss., ≥98 % Al₂O₃ basis): silica gel (SIGMA-ALDRICH, Silica gel, high-purity grade (Davisil Grade 633), pore size 60 Å, 200 – 425 mesh particle size) chromatography column. Aliphatic hydrocarbons were eluted with 5 mL of n-hexane; PAHs were eluted with 10 mL of n-hexane/dichloromethane (1:1 v/v). The fractions were concentrated to 1 mL under a stream of pure nitrogen and stored at 4 °C prior to instrumental analysis.

PAH concentration was determined using the gas chromatograph Shimadzu GC-2010 Plus with the Flame-Ionization Detector (GC-FID) and the Shimadzu 7683 Auto-sampler. The chromatograph was calibrated with Polynuclear Aromatic Hydrocarbons Mix analytical standard, 2000 µg/mL each component in methylene chloride: benzene (1:1). The chromatography column: Rxi®-1ms, Crossbond® 100 % dimethylpolysiloxane, length – 20 m, diameter – 0.18 mm, 0.18 µm df. Temperature was set up from 55 to 300 °C at the rate of 10 °C per minute and was maintained at 300 °C for 15 minutes. Carrier gases – helium (0.99 mL/min). The detector temperature is 320 °C.

2.3. Statistical Analysis

To assess environmental conditions (pH, depth, temperature, total organic carbon, and dissolved oxygen concentration) on the distribution of PAH was used multivariate statistics, canonical correspondence analysis (CCA) with R-studio (0.97.248) program.

2.4. Calculation of results

The value of PAH vertical diffusion was calculated as follows:

$$V_D = \frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right) \quad (1)$$

Here V_D is vertical diffusion rate of PAH, C is the concentration of PAH; D_z is the diffusion coefficient in the z direction.

The vertical diffusion coefficient can be expressed as the function of turbulent eddy viscosity:

$$D_z = \frac{v_e}{\sigma_{\varphi z}} = \frac{v}{\sigma_{\varphi z}} + \frac{v_t}{\sigma_{\varphi z}} \quad (2)$$

in which v , v_t and v_e are the kinematic molecular viscosity, kinematic turbulent viscosity and kinematic effective viscosity, respectively; $\sigma_{\varphi z}$ is the turbulent Schmidt number.

Based on the mixing length turbulent model the turbulent viscosity v_t can be expressed as:

$$v_z = \rho l_m^2 \left| \frac{\sigma U}{\sigma z} \right| \quad (3)$$

where l_m is mixing length in the oil–water flow. It can be defined as:

$$\frac{l_m}{l_{m0}} = (1 + \beta R_i)^{0.5} \quad (4)$$

where $\beta=20$; l_{m0} is the natural mixing length, R_i is Richardson number, which can be expressed as:

$$R_i = -\frac{g}{\rho} \frac{\partial \rho / \partial z}{(\partial U / \partial z)^2} \quad (5)$$

For the turbulent Schmidt number $\sigma_{\varphi z}$, the buoyancy influence needs to be considered, and this can be accounted for by the Munk–Anderson formula:

$$\frac{\sigma_{\varphi z}}{\sigma_{\varphi 0}} = \frac{(1 + 3.33 R_i)^{-1.5}}{(1 + 10 R_i)^{0.5}} \quad (6)$$

where $\sigma_{\varphi 0} = 1.0$. After obtaining v_z and $\sigma_{\varphi z}$, the vertical diffusion coefficient can be obtained.

3. Results and discussion

After 2 weeks, under in vitro experimental conditions in the seawater, low-molecular mass polycyclic hydrocarbons *Naph*, *Phe* and *Antr*, which diverged from the oil film, were noticed. High-molecular mass polycyclic hydrocarbons were not detected during the experiment.

An individual and the total PAHs were determined in the dissolved and the suspended phases. During the research, the following PAHs with 2 – 6 aromatic rings, which released from the oil film, were determined: naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1.2.3-c,d) pyrene, benzo(ghi)perylene.

Distribution of PAHs, which released from the oil film, in the dissolved and the suspended phases in different period after the spill is provided in the Figure 1.

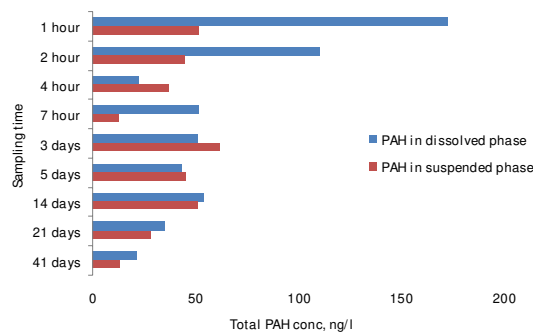


Figure 1. Distribution of PAH in the dissolved and suspended phases in the surface water layer

The figure describes PAH distribution in the water layer under the oil film; the figure also presents the total values of PAHs concentrations. The total concentration of PAHs ranges from 21.4 ng/L to 194.7 ng/L in the dissolved phase and from 5.1 ng/L to 61.9 ng/L in the suspended phase. Due to high hydrophobicity of PAHs, the major part of them should be found in the suspended phase; however, in the carried out research, a larger part of PAHs was found in the dissolved phase. As it can be seen in Figure 1 that release of PAHs from the film starts immediately after spill. As the research was carried out under laboratory conditions, PAH release was not affected by hydrologic factors (waves, wind and

flows), there was no dispersion of the oil film and it could result in slowdown of PAH release from the film.

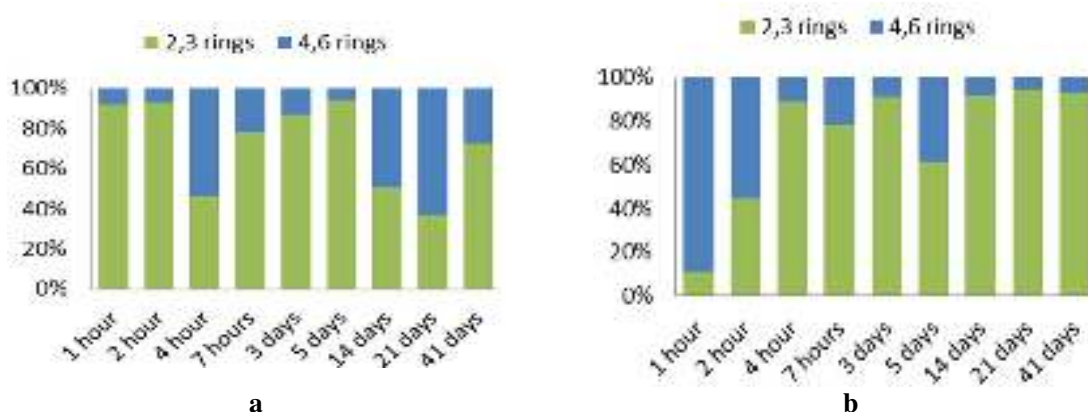


Figure 2. Distribution of 2-3 and 4-6-ring PAHs a) in the dissolved phase, b) in the suspended phase

When analysing qualitative distribution of PAHs (Figure 2), 2,3-ring PAHs dominate in the dissolved phase and they comprise from 45 % to 94 % of all PAHs released during full research period. 4,6-ring PAHs are found in smaller concentrations in the dissolved phase. In some samples, they make even less than 6 % of all PAH. Due to relatively low water-solubility of PAHs and possible desorption from the suspended phase, higher concentration of low-molecular-weight PAHs (2 – 3 rings) can be expected in the dissolved phase. Naphthalene, Phenanthrene and Anthracene make 61 % of all PAH found in the dissolved phase during 1st hour.

To evaluate the effect of environmental conditions for PAH distribution, canonical correspondence analysis (CCA, R-studio) was applied. Based on CCA analysis (Figure 3), environmental characteristics up to 54 % explained variations of PAH concentrations in the water depth. Statistically significant factors were: TOC ($F=93.2$; $p=0.001$), time ($F=57.2$; $p=0.001$), temperature ($F=18.9$; $p=0.001$), pH ($F=16.1$; $p=0.001$). Positive correlation has been estimated between *Naph* and temperature, *Naph* and TOC and negative correlation between *Naph* and time. *Phe* correlated negatively with temperature and TOC and correlated positively with time. Positive correlation was determined between *Antr* and pH, and negative correlations were observed between *Antr* and depth and between *Antr* and dissolved oxygen.

pH of the seawater in the Baltic sea usually varies between 8.1 and 8.3; however, it can vary from 7.5 to 8.3. pH effects speciation of chemical substances, other chemical reactions, coagulation, the interaction of dissolved organic materials (DOM) as well as the interaction of non-polar chemical substances with DOM and other pretreatment processes [16]. Figure 4 describes distribution of *Antr* in the water depth at different pH. The *Antr* concentrations at the upper water layer statistically differ from concentrations at the demersal layer ($r^2=0.77$, $p<0.001$ when $pH=7$; $r^2=0.98$, $p<0.001$ when $pH=3$). At both $pH=3$ and $pH=7$, higher *Antr* concentrations can be observed in the upper water layer and it may be explained by low *Antr* solubility in water ($W_{sol}=0.04$ mg/L). Compounds less soluble in water can be found in the deep-water layers more seldom in comparison with the upper water layer [17]. However, at $pH=3$, smaller *Antr* concentrations can be found in the demersal layer than at $pH=7$. It could be explained by the fact that biotic transportation of hydrocarbons decreases in the acidulated water. Also, carboxyl functional groups increase polarity of organic macromolecules and increase their hydrophobic [18]; moreover, low pH increases accumulation of organic substance [19], what could condition smaller concentrations in the demersal layer.

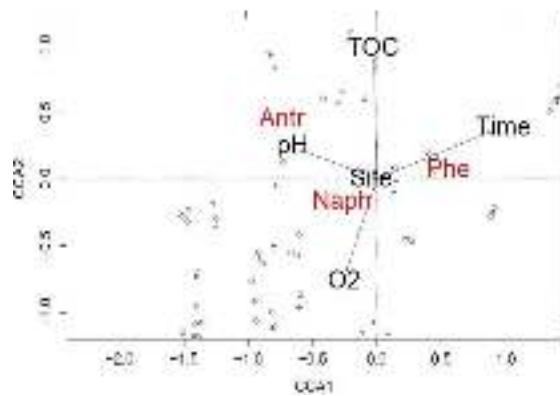


Figure 3. Results of canonical correspondence analysis: environmental factors (pH, depth, total organic carbon (TOC) and dissolved oxygen (O₂) relationship with the concentration of PAH: naphthalene (*Naph*), phenanthrene (*Phe*), anthracene (*Antr*).

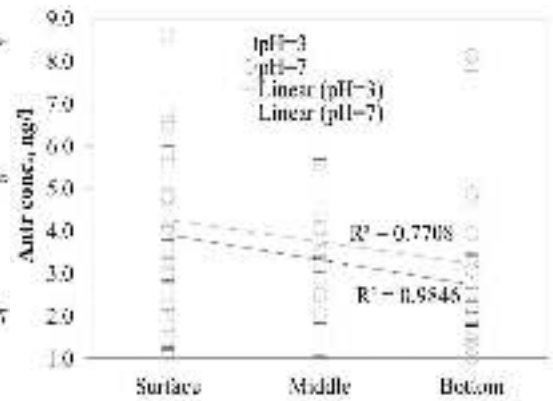
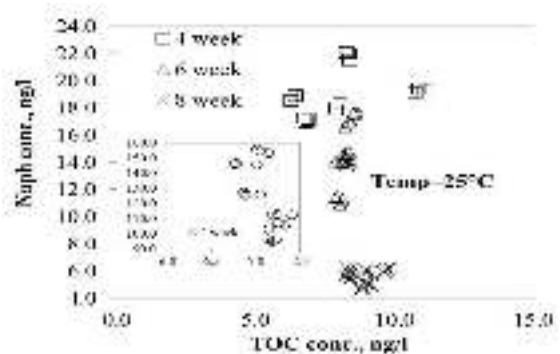
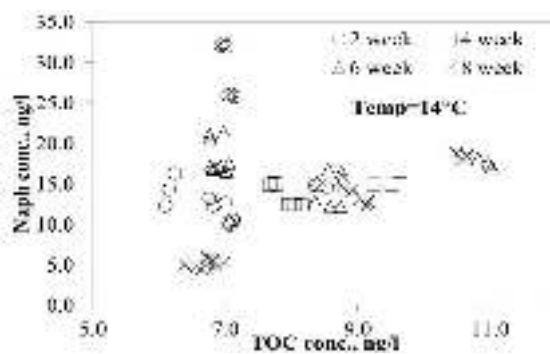


Figure 4. Distribution of *Antr* concentrations at different depths, at pH = 3 and pH = 7

* The measurements are marked by circles

Temperature directly affects physical-chemical properties of petroleum hydrocarbons, such as viscosity, diffusion, evaporation, and it changes oil composition and biological accessibility of water-soluble compounds [20]. Concentration of individual PAHs increases in the seawater in the event of increasing temperature and decreasing salinity but solubility of each PAH changes differently [21]. Changes of temperature and salinity effect differently solubility of individual PAH in the seawater [22]. Though there is general tendency that, in the event of higher temperature, concentration of PAH in the seawater is higher, however, this tendency is more typical for heavy compounds, such as fluorene, phenanthrene, methyl phenanthrene and dibenzotiofene [22]. Thus, significant increase of *Naph* concentration, at the temperature of 25 °C, can be noticed only in the second week. It can be also seen that *Naph* concentration is decreasing in the course of time. Concentration of total organic carbon (TOC) in the water shows similar spatial variation of PAH and is important factor in determination of PAH behaviour [23].



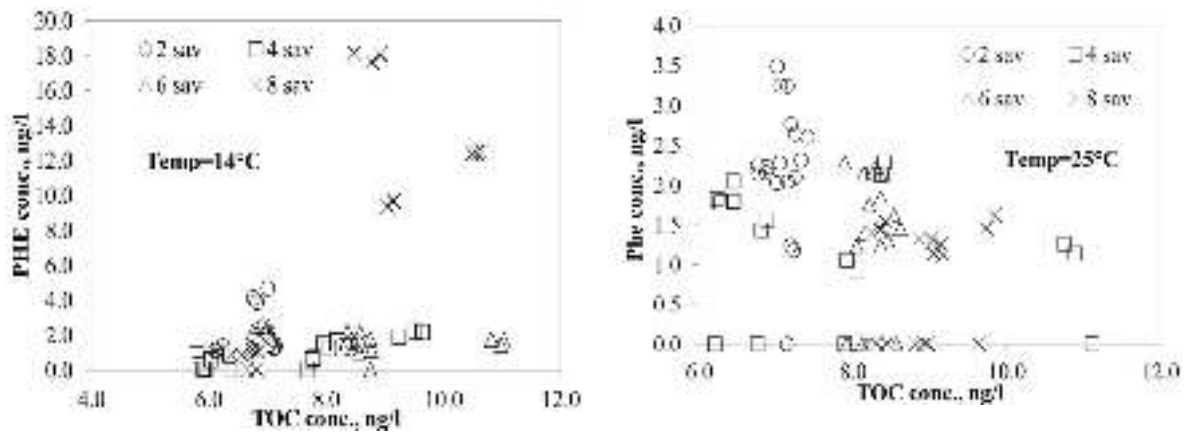
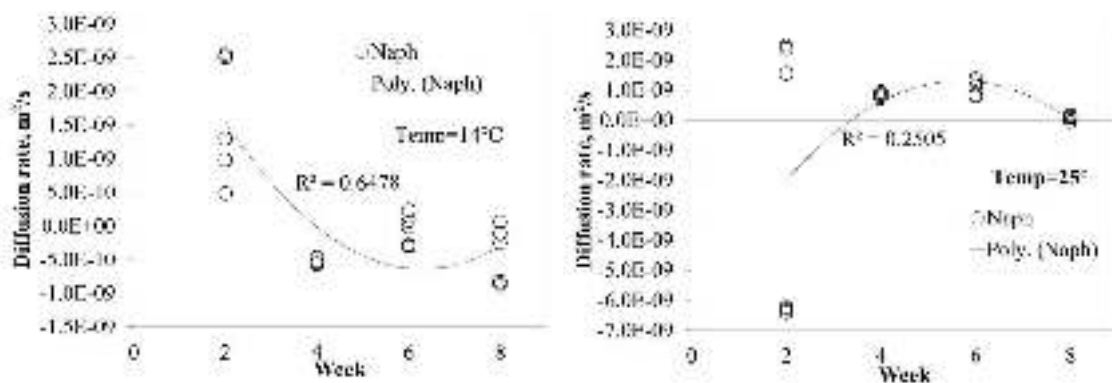


Figure 5. Dependence of *Naph* and *Phe* on TOC at temperatures of 14°C and 25°C

As it is seen from the Figure 5, relation among *Naph*, *Phe* and TOC at the temperature of 14 °C is very complicated for first weeks; low correlation rate ($r < 0.5$) shows deviations from linear dependence. It shows that TOC could become the second factor controlling behaviour of *Naph* and *Phe*. That could be conditioned by other factors, e. g. desorption, amount of fraction lipids or the phase of suspended fractions, which could affect concentration of the dissolved phase PAH [23, 24]. However, in the Figure 6, strong positive correlation among *Naph*, *Phe* and TOC can be noticed. At the temperature of 25 °C, relation among *Naph*, *Phe* and TOC gets totally complicated, there is no clear correlation. Due to increased temperature, processes of sorption could get faster [25] and higher PAH concentration could occur in the phase of suspended fractions. That could be also reasoned by distribution coefficients for octanol-water ($\log K_{OW\ Naph} = 3.37$; $\log K_{OW\ Phe} = 4.57$), which evaluate their solubility in water and organic phases. In the event of increase of K_{ow} , solubility in water decreases; it reasons higher sorption of hydrocarbons in the fractions and/or distribution in non-water phase [26].



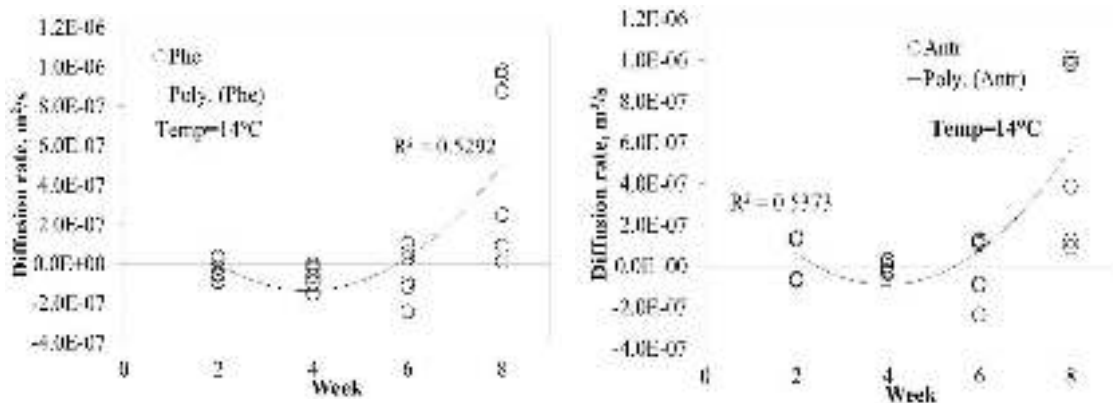


Figure 6. Diffusion rates of Naph, Phe, Antr

Knowledge of molecular diffusion is the base in describing processes that control PAH routes and their distribution in environment [27]. Experimental data show that diffusion of compounds strictly depends on the molecular volume as well as on temperature and medium viscosity wherein the compound diffuses [27]. Diffusion coefficient in the water gets up when temperature increases, and it decreases together with the molecular volume [27].

However, within the second week, the average diffusion rate of *Naph* ($-2.1 \cdot 10^{-9} \text{ m}^2/\text{s}$), at the temperature of 25 °C, is low in comparison with the diffusion rate ($1.7 \cdot 10^{-9} \text{ m}^2/\text{s}$) at the temperature of 14 °C. It could be explained by the fact that during the second week at a higher temperature there was more intensive *Naph* diffusion from the oil film into water. At the temperature of 14 °C, faster diffusion of *Naph* from the oil film into water is going during the fourth week and later. Thus, it could be stated that, at a higher temperature, *Naph* diffusion from the oil film into water is going faster at the beginning of spill and is getting slower in the course of time. The diffusion rate is inversely proportional to the medium viscosity. When PAH diffusion rate in non-water phase (NVP) is a limiting factor in transfer of mass from NVP into water, PAH diffusion controls general solubility rate of PAH [28]. Therefore, slow PAH diffusion conditions slow PAH solubility.

In the provided graphs (Figure 4), it can be seen that diffusion rates of *Phe* and *Antr* vary similarly in the course of time. Diffusion rates of *Phe* and *Antr* ($4.97 \cdot 10^{-6} \text{ m}^2/\text{s}$ and $5.04 \cdot 10^{-6} \text{ m}^2/\text{s}$ respectively), which are provided in the literature [16] and were estimated applying Taylor dispersion method, also are similar; however, diffusion data obtained during our experiment are a few times lower due to constant diffusion of PAH from the oil film into water. It could level PAH concentrations all over the water depth and at particular moments to provide higher PAH concentrations in the upper layer than in the demersal one.

4. Conclusions

During the experiment, low-molecular mass polycyclic hydrocarbons *Naph*, *Phe* and *Antr*, diverged from the oil film, were being observed for 2 weeks. High-molecular mass polycyclic hydrocarbons were not detected during the experiment.

Based on CCA analysis, environmental characteristics explain up to 54 % of variations of PAH concentrations in different water depth. Statistically meaningful environmental factors were: TOC ($F=93.2$; $p=0.001$), time ($F=57.2$; $p=0.001$), temperature ($F=18.9$; $p=0.001$), pH ($F=16.1$; $p=0.001$).

Higher concentrations of *Antr* can be detected in the upper water layer at both water pH=3, and pH=7; it can be explained by low solubility of *Antr* in water ($W_{\text{sol}}=0.04 \text{ mg/L}$). However, in the demersal layer, lower concentrations of *Antr* can be detected at pH=3 than at pH=7.

Relation among *Naph*, *Phe* and TOC at the temperature of 14 °C was extremely complicated for first weeks, and low correlation rate ($r < 0.5$) shows deviations from linear dependence. In the event of

temperature of 25 °C, relation among *Naph*, *Phe* and TOC becomes totally complicated; there is no pronounced correlation among them. Due to increased temperature, sorption processes [25] could get faster and higher PAH concentration could distribute in the phase of suspended fractions.

The average rate of *Naph* diffusion ($-2.1 \cdot 10^{-9}$ m²/s) at the temperature of 25 °C is very low in comparison with the diffusion rate ($1.7 \cdot 10^{-9}$ m²/s) at the temperature of 14 °C. It could be explained by the fact that during the second week, at a higher temperature, there was more intensive *Naph* diffusion from the oil film into water. At the temperature of 14 °C, faster *Naph* diffusion from the oil film into water is going during the fourth week and later. Therefore, it can be stated that in the event of higher temperature *Naph* diffusion from the oil film into water is going faster at the beginning of spill and is getting slower in the course of time.

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