


16th INTERNATIONAL MULTIDISCIPLINARY
SCIENTIFIC GEOCONFERENCE
SGEM 2016

Book 5
Ecology, Economics, Education and Legislation

CONFERENCE PROCEEDINGS
Volume II



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ENVIRONMENTAL PROTECTION

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POLLUTION OF GROUNDS WITH OIL AND PETROLEUM PRODUCTS FROM THE POINT OF VIEW OF SYNERGETICS (KINETIC APPROACH)

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ABSTRACT

Hydrocarbon pollution of environments is the one of most distributed and at the same time not enough studied types of anthropogenic influences. The high intensity of geo- and biochemical processes, flows of the matter and energy connecting the hydrocarbon geotechnical system (HGS) with the external environment determines the necessity of use of the kinetic non-equilibrium approach for the forecast of fate of the polluting substances. Interaction between the intensive and extensive parameters of the HGS forms the centers of the development of kinetic processes (attractors) that determine the direction of the degradation of oil and petroleum products.

Pollution processes and transformation of hydrocarbons in soils and grounds are fundamentally different. We consider the soils as a natural filter, and this is justified by the calculations of the kinetic of formation of different forms of compounds in vertical and lateral migration flows. The process of dispersion of the hydrocarbon pollution is multidirectional in space and time and it is characterized by various speeds of mobilization, immobilization and remobilization of hydrocarbons. The synergetic basis of the mechanical and diffuse forms of the migration of the hydrocarbon pollution is presented in the models as an interaction between the initial liquid-phase, water-soluble, exchange and fixed forms of hydrocarbons.

A complex of kinetic models of destruction of oil compounds in the natural environments was of considered. They show different fate of compounds depending on the type of conditions and the defined ways of degradation and allow more precisely forecast the processes of pollution/ self-purification of environments.

Processes of the natural destruction of oil are inert in the time, but from energy and end results side they prevail over all the artificial influences. Hydrocarbon pollution is non-equilibria on its nature due to the interaction of the external environment and internal processes and has an autowave character. The main driving force of disintegration (even for the persistent compounds) are water and microorganisms due to multistage transformation of hydrocarbons with participation of live substance.

Keywords: Hydrocarbon pollution, petroleum products, self-organization, kinetic, model

INTRODUCTION

Technogenesis is a continuous self-organization of the local pollution zones (genetic structuration) with the differentiation of the substances (hydrocarbons and another pollutions) in time in vertical and areal directions. According to the H. Haken's [3] definition, self-organization are the spasmodic changes of a qualitative and quantitative state of properties of structures, or of the "stable" communications (invariants of the system). According to L. Boltzmann, the structural properties, or the complexity of the system can be estimated using the entropy or the difference of entropies in the processes. Difference between the entropies of distribution of the pollution is testified to the heterogeneity of the physical and chemical processes of the interaction of the pollutant with the environment having different intensities.

The external environment towards to the technogenic systems develops according to the own laws and will hinder to the another way of the development of the emerging or forming at the time in it hydrocarbon technogenic system. This system must accept the conditions of the environment, in particular the same natural geochemical zonality. This initial position postulates the genetic identity of the evolution stages of both the systems. But the processes of the evolution of technogenic systems are incommensurably quicker because the influence on the external environment is more intensive. The internal (technogenic) system doesn't have enough time to adapt to the external environment. So, the alien to the nature substances with the maximum of the variation of the properties, which are able to the bifurcation of the "isolated" processes occur.

Self-organization is based on the complex of the underlying conditions. One of them is a non-equilibria ordering of the dynamic systems (the time category), created because of the cooperative interactions, including the superposition interactions (acting jointly, differently directed and inadequate on the force and time). Such interactions create a dispersion of the polluting substances, coming into the "alien" environment as the response and give rise to the formation of new subsidiaries subsystems. Their formation occurs from the active centers; on their properties these centers differ from the centers of the environment (initial). These centers and the secondary substances can be generators of the occurrence of the more toxic and more aggressive components of the hydrocarbon technogenic systems.

Occurrence of the intermediate compounds in process of the transformation of oil and petroleum products is one of the most actual problems of their identification having the global scientific level. Therefore, from the position of kinetics, a lot of attention should be paid to these processes at the modeling the interaction of the hydrocarbon pollutants with the natural environments.

It is obvious that the natural systems are multi-component. It is possible to conditionally consider the internal and the external multicomponent character. The first are the microscale (and in some measure mesoscale) heterogeneity: for example, the composition of dispersed soils of aeration zone, where the main sorbents are clay minerals (montmorillonite, hydromica, kaolinite, chlorite, etc.). The sorption capacity of

the inorganic pollutants is selectively relative to the large size cations. It is well explained by the differences in the radii of the hydrated ions, their polarizability and structural features. At the same time, the internal multicomponent character is inherent in the very pollutants, especially organic substances. Interaction with the pollutant at this level of environment creates an imbalance in local points (attractors). It is identical to the variety or the creation of phase portraits of interaction between the components of the geological environment with petroleum products at the microlevels.

Interaction of the emerging systems occurs discontinuously and discretely in attractors. In our opinion, in such a way the zones of the pollution are forming in media, so the distribution of the hydrocarbons initially occurs chaotic, and after that the system goes into the ordering stage. Our calculations of the entropy of interaction of various types of oil with the categories of soils and grounds, including peat, quantitatively confirm the provisions cited above (Fig. 1).

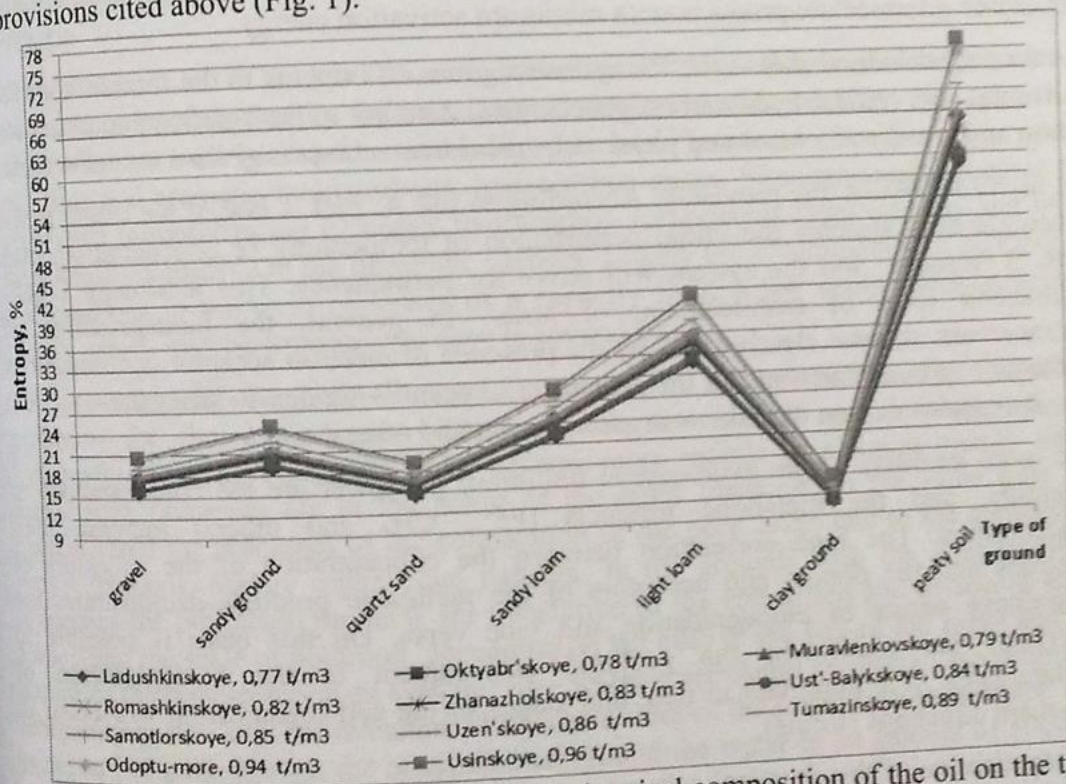


Fig.1. The dependence of the entropy of the chemical composition of the oil on the type of ground

For oil and petroleum products, the sorption processes are controlled by their mineral composition (so, density, viscosity etc.), mechanical composition of the grounds and humidity. Sorption on the disperse soil/ grounds starts from the liquid phase even if the petroleum products are in the dissolved state. At the same time, the greatest activity is shown by polar components of hydrocarbons according to the following scheme: olefins → aromatic hydrocarbons → cycloparaffins → paraffins [4].

There has been increasing role of living matter and products of its life activity in the processes of transformation of hydrocarbons. For example, at the oil pollution of soils and grounds the role of the organic substances of non-humic nature increases sharply. This leads to the formation and conservation of the complex components, that are difficult identified in the natural media. These compounds can be more toxic and

aggressive than the initial substances [1, 2, 6, 8]. There are ketones, alcohols, acids having varying degree of toxicity and the lifetime in the environments. It is believed that the hydrocarbons up to C₂₀ are most susceptible to biodegradation, and this process is realized in the following order: *n-paraffins* → *cycloparaffins* → *naphthenes* → *aromatic hydrocarbons*.

Chemical reactions in the inanimate nature need significant more quantity of the energy to carry them out than the living systems. The same products of the reactions occurring in the multistage processes involving living matter need much less energy than in the reactions without its participation. The activity of the reactions with the participation of living matter is fundamentally different from how the processes take place in the "non-living world." Biochemical processes like "bypass" high activation barriers characteristic for the chemical reactions without the living organisms, and the one-step process is replaced by multiple transformation through a series of transitions and metastable intermediate products with minimum activation energy.

We do not exclude, that it is the living matter gives an impetus to the formation of the horizontal and vertical hydrocarbon geochemical zonality in the aeration and saturation zones, and gravity processes and physicochemical interactions is given a secondary role.

Let us try to justify this provision. According to the A. Fick's law, if we create in the nonequilibrium systems the initial perturbation of temperature or concentration, over time, it "resolve" and the system will strive for permanence. This is already a well-established form of manifestation of order. In general, the biodegradation of hydrocarbons scheme clearly fixed by the presence of electron acceptor concentrations in the soil (ground) or water in the sequence: oxygen → nitrates → manganese → iron → sulphates → carbon dioxide → organic carbon and others.

The more intensive is the hydrocarbon pollution, the lower are the concentrations of acceptors, and the metabolic products (Fe²⁺, CH₄ and others) increase their concentration. The high correlation between the concentration of the acceptors of electrons and the donors and acceptors of the metabolic products demonstrates the progressive nature of biodegradation and vice versa. On this basis is possible to determine the ability of the geologic environment to the biodegradation of contaminants. It is important to note that stages of the self-organization will occur in two main directions (forms).

1. Organization of the chemical substances on the principle "from the short-living – to the long living". Such chains are different on the composition in the entrapped air, in vertical and horizontal flows of moisture and, actually, in the porous and fractured environments of soils and rocks.
2. Manifestation of the accumulation of the concentrations of chemical elements on the geochemical barriers (contrast forms), in the form of stratigraphic units with a smooth rise and fall of concentration. The more the interaction time, the clearer will be shown geochemical zonality and azonality.

The fractioning in the system "hydrocarbons – rocks" is that in rocks are predominantly accumulated the compounds of high molecular weight (resins, asphaltenes and others), and into the aquifers fall such compounds as benzene, toluene, xylene, etc. having a relatively high solubility.

More stronger connections and, consequently, structuring will manifest in the subsoil layer of vadose zone and to the spread of groundwater. That means that the diffusion in the fractal medium (and to such one can be attributed all the natural reservoirs) occurs not like in the conventional continuous medium. The dispersibility of the rock and chaotic fracture structure complicate the advancement of particles and slow down the diffusion. The deviation of the natural parameters of the diffusion in the fractals from that one in the models is so significant that it does not satisfy the classical law of A. Fick and, consequently, the diffusion equation. The situation will not be saved with the introduction of the variable coefficient of the diffusion depending of the dimension of the pore space. There is need for the use of integral-differential equation containing a new unusual object - a derivative (in time) of fractional order related to the fractal dimension of the media. Thus, the "impurities decay functions" *become the leading role* in the knowledge of the processes of self-organization in the hydrocarbon technogenic systems.

Under the condition of the law filtration properties of the grounds occurs the penetration of the moving low-density hydrocarbons, which are dissolved in the aggressive wastewater as well as liquid commodity petroleum products (free-flowing), cycloparaffins and aromatic hydrocarbons, hydrocarbon gases. Simultaneously, occurs the prolonged immobilization of heavy hydrocarbon components (fuel oil, oils and other high-density liquids). On the lithologic barriers is likely the accumulation of all kinds of hydrocarbons in the form of lenses of a capacity from a few centimeters to several meters, which may be from several days to several years.

The grounds with the high filtration properties are the sources of the secondary pollution for the groundwater. There is the dissolution and leaching of the hydrocarbons in these grounds (they became more mobile as a liquid phase). More active such processes are in the zones of the rapid filtration. In the same time are characterized the processes of the colmatation of the pore space due to the sorption of heavy fractions, mainly asphalt and paraffin. In the grounds with the high filtration properties the petroleum products are transferred in the emulsified and dissolved state. Expanding the scale of pollution, depending on the ratio of the size of the zones and the nature of the three-component system "air - water - petroleum products." According to laboratory data to start the reduction of concentrations of the hydrocarbons in water, it is necessary to pass through the contaminated ground the water in an amount of 500-600 pore volumes.

Here is an example. It is believed that the under the underground anaerobic conditions the processes of natural biodegradation of petroleum products are very slowly. It is confirmed by the facts: the pollution and self-cleaning of karst rock massifs last centuries long. Studies in recent years showed that nitrate ions can act as an electron acceptor, and after their exhaustion - iron and sulphate ions, always present in the groundwater. This has led the authors [5] to conclude that the biodegradation process in anaerobic conditions occur as effectively as aerobic. On the example of the former military base (airfield) in the Czech Republic was demonstrated a change in gross of the content of petroleum products in one of the wells where the monitoring of contaminated groundwater was organized (Fig. 2).

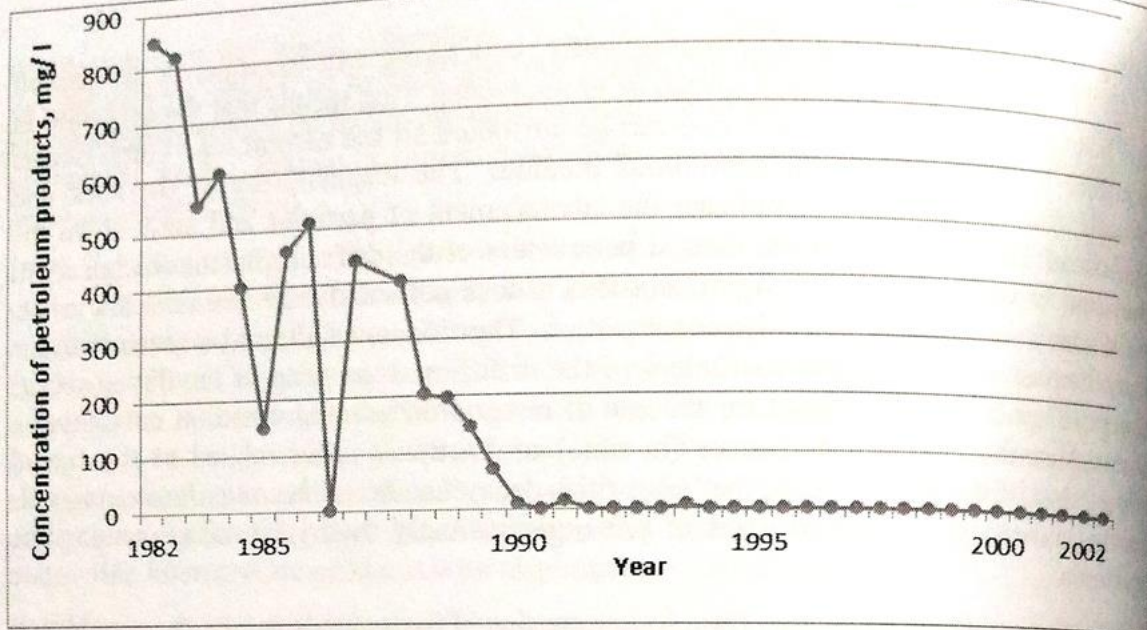


Fig. 2. Dynamics of concentration of petroleum products according to the monitoring well [5]

From the Earth's surface the friable deposits of quarternary age spread at a depth of 5-6 m by crystal rocks with the jointing decreasing with a depth. Underground waters lie at depths of 3-5 m and are dated for friable quarternary rocks and a zone of a jointing in the crystal basis. In our opinion, at such geological structure the possibility of migration of the dissolved oil products in crystal rocks with their subsequent deposition isn't excluded.

The geochemical zonality is justified by the long-term research of hydrocarbon pollution of the geological environment on the site of Bemidji (USA) [2]. The detailed research during more than 20 years showed the ratio of the anaerobic and aerobic degradation of the hydrocarbon pollutants in the geological environment as 60:40. Thus for typical representatives of the anaerobic conditions the reduction of manganese is up to 5%, iron 19% and 36% is methanogenesis.

Detailed models of processes of biodegradation of petroleum products require the analysis of the kinetics of degradation of pollutants. It is known that as the oil pollution markers are widely used PAH, which clearly record the origin and age of the contamination. The behavior of the living matter is similar to the catalyst in chemical reactions. Using the stoichiometric equations and Gibbs' energy calculations, we can make assessments of the rate of degradation of PAHs (as marker compounds) and, therefore, of the selfpurification of the geological environment. So, one of the examples of the calculation of PAH biodegradation was shown in [7] for naphthalene as a most bioavailable substance.

CONCLUSION

So stratigraphic unit as an integral structure is an indispensable element of the existence of any ecological system and the most important object of study in the identification of pollution of the geological environment of the micro to the macro level. This is the most effective in terms of energy expenditure form of existence of matter; it is minidissipative structural substance.

Stratification in time and space (as the self-regulation cycles) is the most perfect structure for displaying of the dynamics of interaction of substances (including various genetic nature), energy and information.

Fluctuations always exist in the physical, chemical, biological, and others systems. The calculations show that the inserted fluctuations unlike the equilibrium processes studied in classical thermodynamics, determine all the future fate of the nonlinear system.

Autowave processes, inherent in almost all natural systems, form a progressive or regressive nature of biodegradation of pollutants due to the ordination of factors leading to differentiation and activity of living matter in time and space.

This feature of the development of hydrocarbon systems is illustrated using the kinetic models of hydrocarbon contaminations and degradation confirmed by field experiments fixing the decrease of the concentrations of the electron donors and acceptors involved in the oxidation of oil components in soil both under aerobic and anaerobic conditions.

ACKNOWLEDGEMENTS

The material was prepared with funding from the Ministry of Education and Science of Russia in the framework of the project of the Federal Target Program "Research and development on priority directions of scientific-technological complex of Russia for 2014-2020", "Development of the expert system of rehabilitation of the geological environment polluted with oil products, based on the principles of self-organization for the territories of CIS countries "(project ID RFMEFI58414X0011).

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**ECOLOGY, ECONOMICS, EDUCATION AND LEGISLATION
CONFERENCE PROCEEDINGS
VOLUME II**

ECOLOGY AND ENVIRONMENTAL PROTECTION

**30 June – 6 July, 2016
Albena, Bulgaria**

HYDROCARBON FLOWS IN THE SEDIMENTS OF WATER BODIES: APPROACHES TO THE IDENTIFICATION OF THE ORIGIN OF POLLUTION

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ABSTRACT

The income of oil and products of its processing into the environments is really significant. To organize the monitoring of the marine environment and assessment of the contamination processes different approaches are developed allowing the identification of the source of pollution and estimation of its role in the formation of the non-equilibrium system of the sediments in the water bodies.

The wide used method of the identification of sources of the hydrocarbon pollution is calculation of indicator ratios of polycyclic aromatic hydrocarbons (PAH). Because of the existence of PAH-isomers with different properties coming from different sources, it is possible to identify the genesis of the pollution and in some cases its' age. In our study we test the most wide used ratios and examine the possibility of its use for the purposes of the identification of hydrocarbon flows.

Calculations showed that the analysis of individual indicator ratios sufficiently informative. For some ratios was shown significant difference of calculated values from presented in the literature critical values. Maximal efficient is the analyses of a complex of ratios. So, it is possible to study the behavior of hydrocarbon flows in sediments.

In contrast to existing perceptions of sediments as the storage medium, we propose to consider them as non-equilibrium geochemical system with a continuous exchange of matter and energy between the components and supersystem. When interpreting the indicator ratios it is necessary to make correctives taken into account methods used for extraction and detection of PAHs, the specificity of the polluted environment, the age of pollution, nature of the source of PAHs, their concentration and behavior models.

Keywords: hydrocarbon flows, oil, PAH, indicator ratio, sediments

INTRODUCTION

The income of the hydrocarbon pollutants into water bodies reaches significant volumes in many regions of the world, so this problem belongs to the priorities. The monitoring

of water bodies mainly gives assessment to the water media; to the sediments is paid far less attention at all kinds of the ecological/ environmental studies. At the same time, the data about the sources and character of the pollutants as well as processes of their transformation is necessary. On this basis it is possible to make decisions about the acceptability of environmental loads or about the necessity of their regulation. Thus, it is necessary to take into account the specific character of bottom sediments as the environment, taking over a significant portion of the hydrocarbon contamination.

The sediments are a conservative system that stores the information about a lot of processes occurring in the water body, including the technogenic. Traditionally less attention is paid to the organic pollutants in Russia, not to mention Persistent Organic Pollutants (POPs) and polyaromatic hydrocarbons (PAHs), that are potent carcinogens. These substances are a kind of molecular markers reflecting pollution and self-purification of the water reservoir, so they are an object of a careful study. Therefore, into the circulation was introduced the concept of *aquatic geosystem* [3] as a unified space in which the components of water bodies are in the system communication with each other. We can present such a unity in the form of the following system (Fig. 1).

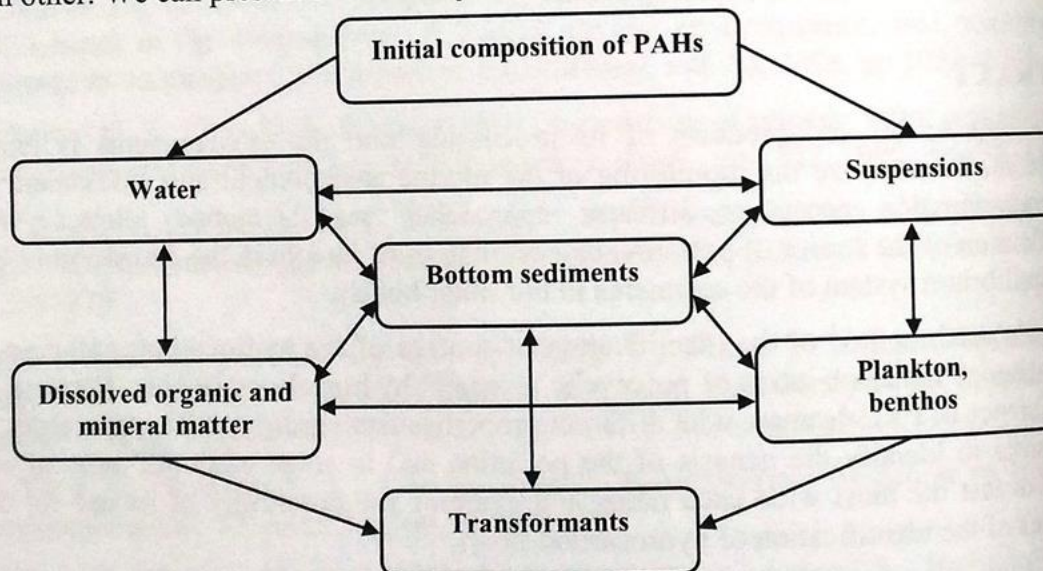


Fig. 1. Sediments as a nonequilibrium system

In Russia, the behavior of PAHs in the sediments of Arctic seas is mostly investigated, where according [2] the significant variations of PAH concentrations was fixed: 20 (background) ng/g to 7500 ng/g (area of Holocene coal-bearing deposits on Spitzbergen). In the areas of obviously expressed technogenic influence (Kola Bay), are fixed total concentrations of PAH till 2500 ng/g. The highest concentrations are characteristic for the fraction 1-10 micron with prevalence of phenanthrene in the sum of PAHs.

PAHs in water. Under the influence of the technogenic activity the mobilization (mechanical, chemical, organogenic) of substances in the solid, liquid and gaseous state occurs, it involves all the stages of the water cycle. The most important source of PAH in the water reservoirs is the atmospheric transfer on the solid particles. PAHs with high molecular weight are adsorbed on the solid particles and transferred on hundreds and thousands km. In many respects the sorption effects depend on the diameter of the particles and on the organic component of the dispersion complex in the suspended

matter. The concentration of the organic component varies from 10 up to 70% and depends on the meteorological conditions. The genesis of the organic component can be natural (fires, dust incoming) or technogenic.

PAHs are characterized by a very low solubility in water, and it decreases with an increase of the molecular weight. The solubility of phenanthrene in the fresh water at 25°C is 1080 µg/dm³ in contrast to that in the saline water 644 [6]. The solubility of PAH correlates with a temperature: for phenanthrene in the fresh water it increases from 423 µg/dm³ at 8.5 °C up to 1277 µg/dm³ at the temperature 29.9 °C. It can indicate the more significant accumulation of PAH in the southern seas in contrast to the polar areas. Sorption on the sediments increases with increasing of salinity and decreasing of temperature.

PAH on organic and mineral suspended matter. PAHs with relative high Henry's constants (naphthalene, fluorene, phenanthrene) evaporate from the water first. PAHs with relative higher molecular weights distribute between the water and solid (particles) or colloid phases. So, the surface and the bottom waters of the Chesapeake bay contains an average 8.71 ng/ dm³ and 14.05 ng/ dm³ of sum of suspended matter where sorbed 18 up to 86% of individual PAHs. The rest PAHs are associated with the dissolved and colloid phases [6]. The common trend for the volumes of PAH, sorbed on the suspended phase is an increase with the increasing of the molecular weight (from 17% in the solid phase for fluorine up to 86% in the solid phase for benzo[k]fluoranthene). The near-surface water with the common content of phenanthrene 0.9 ... 4.9 ng/ dm³ contain 0.46 ... 1.52 ng/ dm³ phenanthrene in the dissolved form; the near-surface water with the concentration of the total benzo[a]pyrene 0.2 ... 0.5 ng/ dm³ contain 0.03 ... 0.06 ng/ dm³ of dissolved benzo[a]pyrene. Thus, the main part of PAHs accumulates on suspended matter and afterwards they are able to go into sediments. For Arctic and Baikal lake this mechanism develops in a specific way: only a small amount of PAHs are dissolved in water and sedimented; the anomalies are possible in the locations of the natural discharge of the hydrocarbons or after the accidents. The accumulation is limited by low temperatures and small amounts of suspended matter with an organic component. The temperature variations create different flows of the matter (suspensions) in space and time. Thus, occurs the disturbance of the dynamic equilibrium of the PAH's concentrations in the system 'water - sediment' due to the emergence of autowave processes from the outside.

The second type of the fluctuations connected with this system is created due to the internal microprocesses, arising in certain points - attractors inside of the system (internal structurization). These processes are resulted by binding of the natural organic colloids in the form of various compounds, for example with PAHs. These associations are caused also by solubility and concentration of slightly soluble hydrophobic organic substances in a water phase and by the molecular mass of PAH.

Thus, the major property of PAHs is their selectivity to the sorption on the solid (organic or mineral) particles, colloids, in biomass depending on the construction of PAH molecule, salinity and temperature.

Of importance are the processes of the removal of the dissolved (colloid) forms of PAH with the subsequent sedimentation to the bottom of water reservoirs and water currents. Taking into account the low solubility of PAHs in water (except of naphthalene), is

possible to say that the processes of hydrolysis and crystalline salting-out (taken into account the exchange reactions) are not the prevalent. At the high mineralization of the waste water (for example, at the dumping of the brines with high concentrations of the petroleum products) is possible the transfer of certain hydrocarbon compounds (inclusive PAHs) into the disperse form with further co-precipitation to the bottom. Taken into account the sorption capability of PAHs, the presence of suspensions in the waste water promotes to the mechanisms of the natural flocculation (removal of PAHs from the solutions). Therefore, their high concentrations in the water environment, including the water extracts from bottom sediments, are improbable.

This point of view is confirmed by the following example. According to M. Yunker [6], all the PAHs with the molecular mass 228-278 was found in dissolved phase of water samples from the interaction zone of the delta area of the Mackenzie river (Beaufort Sea). The presence of the 4-6-ring PAHs shows, that the higher PAHs are transported in the dissolved form by the river, where they became more bioavailable compared to water flow. In the river and on the shelf the total concentration of PAH in the dissolved phase is ca. 1 ng/l, and it varies not significant from season to the season and at the changes of the concentrations of the dissolved particles in the water column. In our opinion, this is a very important conclusion, indicating that the formation of ion-salt composition of river and of PAHs concentrations in natural waters has fundamental differences. In the first case the total mineralization and variability of the chemical composition (including biogenic components) in water are due primarily to the solubility of compounds. In contrast, for the PAHs concentrations the presence of dissolved organic matter, mechanical and organic suspensions, on that they migrate is essential. Therefore, the explanation of the low concentrations of PAHs in water only as a result of their low solubility is at less not legitimately. Thus, the position is confirmed, that was suggested by the Russian researches: the near-delta areas are the marginal filter, able to precipitate almost all pollutants on the border "river – sea".

The role of plankton and benthos in the process of sedimentogenesis of PAH. Bioaccumulation and microbial reduction of PAHs have a leading significance for the quantities of PAHs in the bottom sediments. The accumulation of practically all forms of PAHs for the benthos is common. At the withering occurs the burial with preservation of accumulated substances, including the pollutants. For microbiological substances the recovery of chemicals in a weakly or substantially insoluble forms is typical. Thus, plankton and benthos are the "accumulators" of PAH; they make a very significant contribution to the total pollution of bottom sediments.

PAH accumulation and bioaccumulation in the aqueous environment and in organisms correlate inversely with the potential and ability of the hydrocarbons to metabolize as well as to the chemical transformations. Nevertheless, the role of water despite of the low solubility of PAH is very large in these processes, and determines the selective character of their degradation in all environments. The role of the microflora is huge. In fact, it is the realization of self-purification mechanism of water bodies (self-organization), that allows to create a fundamentally different approach to the assessment and identification of impurities [1, 4]. Virtually all the hydrocarbons undergo the biodegradation.

PAHs in the sediments. According to A.Yu. Opekunov [3], in technogenic silts prevail mainly the reduced forms of bitumoides; this indicates their naphtidogenic nature and

mature petroleum hydrocarbon contamination. When compared with background values in technogenic silts of the identical fractions (it is very important, because the adsorption capacity relative to many pollutants of sediments depends on the mechanical composition), the bitumen concentrations were 4-7 times higher, and hydrocarbons - 6-13 times. The proportion of hydrocarbons in technogenic silts amounts to about 50-70% as opposed to 30-50% in uncontaminated pelites.

The final product of the biodegradation of petroleum products (inclusive PAHs) in the bottom sediments is carbon acid, which can connect with carbonates. These compositions are low permeable and form an interlayer, which prevents the vertical migration of moisture and thus, substances. This contribute to consolidation of the mechanical and material structure of the sediments. In addition, sediment oxidation products (oxykerites and huminokerites) also slow down the exchange between the aqueous environment and the bottom sediments.

According to the common accepted opinion, PAHs differentiate depending on the genesis: for the pyrogenic objects are typically pyrene and benzo[a]pyrene; naphthidogenesis is characterized by the accumulation and transformation of phenanthrene; for the biogenic objects are phenanthrenes, chrysenes and perilenes are representative. In the processes of the technogenic sedimentogenesis can be found practically all the isomers of PAHs, thus the assessment of their indication properties taken into account their stability in the environments is fundamentally important. At the increase of the role of technogenesis, in the composition of PAHs of the bottom sediments we can see the prevalence of the group of kinetic isomers, primarily benzo[a]pyrene, benzo[a]anthracene, anthracene and fluoranthene [4]. For the identification of the origin of PAHs most wide used the indicator ratios of their concentrations calculated for PAHs of the same molecular mass. These are isomers, one part of them are considered as "kinetic" (more active) and another one are the "thermodynamic" (more stable) [6]. The most wide distributed ratios (with the respectively critical values) are the following:

- phenanthrene/ anthracene (Ph/ An): $Ph/ An > 10$ – petrogenic; $Ph/ An < 10$ – pyrogenic;
- anthracene/(sum of isomers with molecular mass 178), $An/(Ph + An)$: $An/(Ph + An) > 0,10$ – petrogenic (diesel oil, shell oil, coal, crude oil); $An/(Ph + An) < 0,10$ – pyrogenic (lignite, emissions of diesel fuel and fuel oil etc.);
- fluoranthene/ pyrene, Flu/ Py : $Flu/ Py > 1$ – petrogenic (Yunker, 2002), $Flu/ Py < 0,4$ – petrogenic [5]; $Flu/ Py < 1$ – pyrogenic [6], $Flu/ Py > 0,4$ – pyrogenic [5];
- fluoranthene/ (fluoranthene + pyrene): $Flu/ (Flu + Py) < 0,50$ – petrogenic (most petroleum products and products of their combustion); $Flu/ (Flu + Py) > 0,50$ – pyrogenic (combustion of kerosene, grass, coal, wood; creosote);
- benzo[a]anthracene/ benzo[a]anthracene + chrysene (triphenylene), $BaA/228$: $BaA/228 < 0,20$ – petrogenic; $BaA/228 > 0,35$ (sometimes $BaA/228 > 0,50$) – pyrogenic;
- indeno(1,2,3-cd)pyrene/ indeno(1,2 3-cd)pyrene + benzo[ghi]perylene, $IP/ (IP + Bghi)$: $IP/ (IP + Bghi) < 0,2$ - petrogenic; $IP/ (IP + Bghi) > 0,5$ burning of grass, wood and coal, wood soot, creosote; $IP/ (IP + Bghi) < 0,5$ fires in the savanna; products of combustion of petroleum products and crude oil etc.

We have used different data about the concentrations of 16 PAHs (the EPA list) in the samples of bottom sediments of creeks (with the division in the fractions of different size), rivers, water areas of ports, bays and estuarine zones (total 57 samples). Influence of technogenesis on these objects is different: from a minimum (the region of Lake Baikal.) to active influences (Taiwan, the area of the seaport; the Persian Gulf after the US military aggression, which led to an environmental disaster in the late 2000s, and other objects.). Of the examined samples minimum concentrations of PAHs are peculiar to the waters of the lake bottom sediments. Baikal; maximum - sediments from contaminated streams in Alabama (fraction of more than 2800 m - large fragments of organic origin). A part of the data are the concentration of PAHs in the sediments of the various fractions (from 45 to 2800 microns). For all the fractions and PAH varieties was shown the decreased capacitive properties in the range of 180-1400 m and two peaks at 1400-2800 with the sharp rise of concentrations on fractions of more than 2800 microns. In the chemical composition there is a prevalence of 3,4-benzopyrene (40 to 2330 $\mu\text{g} / \text{kg}$) and indenopyrene (from 0.9 to 1,774 $\mu\text{g} / \text{kg}$). Thus, the selective adsorption of PAH traced depending on the size of polluted sediment fractions.

For the PAH indicator ratios also revealed the dependence of the values of the particle diameter, which indicates the need to consider the fractional composition of sediments by using indicator ratios (variations are possible up to 1.4 times from the accepted critical indicator values).

Data analysis has shown that different indicator ratios informativeness is different and not always is satisfactory. So, even the traditionally informative ratios $\text{Flu} / (\text{Flu} + \text{Py})$ and $\text{An} / (\text{Ph} + \text{An})$ do not allow confident distinction on pyrogenic and petrogenic groups.

To identify patterns of the genesis and distribution of PAHs, as well as estimating of the informativeness of indicator ratios was used a multivariate statistical analysis. Using principal component analysis was revealed the factor structure of markers and carried out the typification of the objects of sampling. The principal component method revealed substantially the same ability to recognize at such genetic markers as the Ph / An , $\text{Flu} / (\text{Flu} + \text{Ru})$ as well as $\text{BaA} / 228$ and $(\text{Py} + \text{Flu}) / (\text{Chr} + \text{Ph})$.

A clearer genetic division of objects gives a diagram of factor scores in the plane of the first two factors, confirming the presented arguments about the significant differences of PAH content. This diagram allows you to select a group of objects in accordance with the origin of PAH in sediments. Quite clearly stood out the group of man-made sources of PAH (areas of influence of the industrial port and the mouth of the heavily polluted river in Taiwan, specific pollution in the Persian gulf region, locations of oil pollution of rivers and sediments that were formed under the influence of storm water). "Anomalous" were the least contaminated sites - lake sediments in the region. Baikal.

However, calculations of these indices showed that the analysis of individual ratios is insufficiently informative. More objective are the conclusions on the basis of a set of coefficients, using methods of multivariate data analysis. Another solution is the calculation of integrated indicators of origin of PAHs based on concentrations of several compounds.

Also of considerable interest is the analysis of the behavior of PAHs on the geochemical barriers and processes of their transition between the environments in the system "water - bottom sediments". These studies show a picture of the distribution of PAH flows and

allows to estimate the reliability of approaches to identification of the genesis of oil pollution.

CONCLUSION

In contrast to the existing ideas about sediments as the storage medium, the authors propose to consider them as non-equilibrium geochemical system with a continuous exchange of matter and energy between the components and supersystem.

The complexity and diversity of the processes of the genesis of sediments does not allow to use the indicator ratios without a preliminary assessment of their informativeness and to translate mechanically the established boundaries (critical values of ratios). For various geochemical conditions it is required to identify the relevant indicator ratios of PAH. In some cases, it is impossible to unambiguously identify the PAH in sediments as petrogenic or pyrogenic.

For the different natural and technogenic environments should be used the same (universal) values of the indicator ratios. The attempts of the mechanical translation of the presented above critical values for the identification of the genesis of PAHs in different objects showed that in each case is necessary to "customize" them individually [6]. Moreover when interpreting the indicator ratios, it is necessary to make the adjustments and take into account the extraction and analyses methods, properties of the medium being analyzed, the age of pollution, genesis of the source of PAHs, their concentrations and behavior models. Otherwise, a very considerable distortions and errors in determining the source of contamination are possible.

The maximal effect of PAH identification in sediments is achieved when considering a complex of coefficients that must be optimized considering the informativeness of indicators.

Taking into account the possible number of space-time state of environmental components and a variety of conditions and types of sources of exposure in the system "dose - effect" it is necessary to make the corrections in the proposed indicator ratios depending on region and the environmental properties.

ACKNOWLEDGEMENTS

The material is based on the research results of the project 080122-1-274 "Innovative technologies of monitoring of exogenous substances, biomarkers and supertoxicants in objects of environment and human and animal biofluids" with funding of the Peoples' Friendship University of Russia

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Published by STEF92 Technology Ltd., 51 "Alexander Malinov" Blvd., 1712 Sofia, Bulgaria
Total print: 5000

ISBN 978-619-7105-66-7

ISSN 1314-2704

DOI: 10.5593/sgem2016B52

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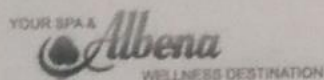
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