Specificity of accumulation of hydrocarbons in various components of geosystems

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Abstract. The results of the analysis of thermodynamic characteristics of the processes of hydrocarbon amassment in the components of geochemical systems are presented (waters, soils, plants and other substances forming ecosystem). The need to use an ideology and apparatus for calculating thermodynamics is due to the complexity and diversity of mass transfer in interacting media. The material and energy flows of marker compounds, polycyclic aromatic hydrocarbons (PAHs), are analyzed: Naphthalene (Naph), Acenaphthene (Ace), Fluorene (Flourene), Phenanthrene (Phen), Anthracene (An), Fluoranthene (Flu), Pyrene (Py), benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbFlu), Benzo[k]fluoranthene (BkFlu), Benzo[a]pyrene (BaP), Benzo[ghi]perylene (Bghi), Dibenzo[a,h]anthracene (DbA), Indeno[1,2-cd]pyrene (Ip). Estimates are obtained of the intensity of PAH concentration processes in geochemical systems in different states from the point of view of stability, from clearly unstable to metastable. The role of living matter in the formation of stability of geochemical systems is revealed.

Introduction

The proposed study focuses on PAHs – very common in the environment, persistent substances able to cause significant negative effects on organisms. At the same time, an important feature of this group of substances is the ability to mark natural and technogenic processes. Analysis of PAH concentrations reflects the hydrocarbon flows in the environment, allows to identify areas of influence of pollution processes. The specific structure of molecules (2 and more benzene rings) determines the hydrophobicity and lipophilicity of molecules and their behaviour in media.

Ordering the movement of organic molecules dissolved in water solutions in the gravitational field creates conditions for their collective behaviour. Coherent motion occurs even in systems that are "sensitive" to weak fluctuations in the gravitational field. This is the reason for the difference in the concentration gradients of hydrocarbons and, as a result, the variation processes in geochemical systems (GCS), acting from outside, and the development of the system itself, depending on the receipt of energy quanta.

According to Buck et al. (1987), systems with a large number of interacting elements naturally evolve to a critical state in which any (even small) event will lead to the

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destruction of the system or a change of state. This principle is the base of our research on the concentration of PAHs through estimates of measures of heterogeneity (entropy) in GCS is based on. Other thermodynamic characteristics have been also calculated for assessing the direction of processes: changes in Gibbs energy (ΔG) and enthalpy (ΔH). The distribution of substances in octanol and water (log Kow) for PAHs was also used, which allows to judge the selective possibility of their movement with solutions in media.

Research methods and objects

A set of the objects for modelling includes 142 genetically different components of GCS:

- a part of the objects can be considered background (samples of water, soil, silt, brine, various parts of hydrobiont plants on the Kerch Peninsula) [1-3];
- samples from areas with an intense technogenic pressure: soils, vegetation, water and bottom sediments of Aojian river and it's estuary (the area of development of the leather industry in China) [4]; soil samples and needles of various plants from regions with different levels of anthropogenic pressure (zone of influence of the Irkutsk aluminium plant, Melnichnaya Pad settlement, villages Moty, Baklashi, Olha) [5]; samples with different levels of anthropogenic pressures in the Arctic and Antarctic regions [6, 7];
- test soil-plant systems (soil - rhizosphere - root - stem): conditionally clean and irrigated with sewage for more than 40 years [8];
- snow samples from the RUDN campus (the territory of Moscow with variable technogenic loads and under the influence of highways) [9].

The migration and accumulation activity was estimated on the basis of concentration coefficients (CC) – the ratios of the concentrations of individual PAHs in an object to the average concentration in a group of genetically similar objects. The calculation was carried out using hierarchical constructions of data structures and formal classification logic (the concept of division of concepts or the logic of a jump in data). Given the heterogeneity of the media, 5 iterations of classification were adopted. For them, in addition to QC, thermodynamic parameters were calculated. Such a set of methods allows us to consider possible variations of PAH fractions in the system of "signs - objects" within the framework of the ideologies of synergetic and formal kinetics.

Results and discussion

Among the probable reasons for the separation of PAHs into groups (fractionations) are the internal physicochemical (molecular) properties. This is a fundamental conclusion that allows one to interpret many processes of concentration of PAHs in media and the conversion of energy from thermodynamic positions. The identification of the structure of PAH bonds is illustrated by the dendrogram of cluster analysis (Fig. 1). PAHs are distributed into groups as a whole according to their mass (respectively, the number of aromatic rings in the molecule, and hence the shape and properties). Thus, the group of the lightest PAHs included Napa, Ace, Fluorene and Py (the latter has 4 rings and is relatively far from the centre of the group). The remaining group of PAHs can be divided into the heaviest (5-6 rings) and relatively lighter (mainly 4-ring). The mobility and migration of PAHs from water media to other media is also due to the synergistic influence of the media themselves-porosity, temperature and lipophilicity, etc. This is confirmed by correlation coefficients (close relationship of physical and chemical characteristics with PAH concentrations).

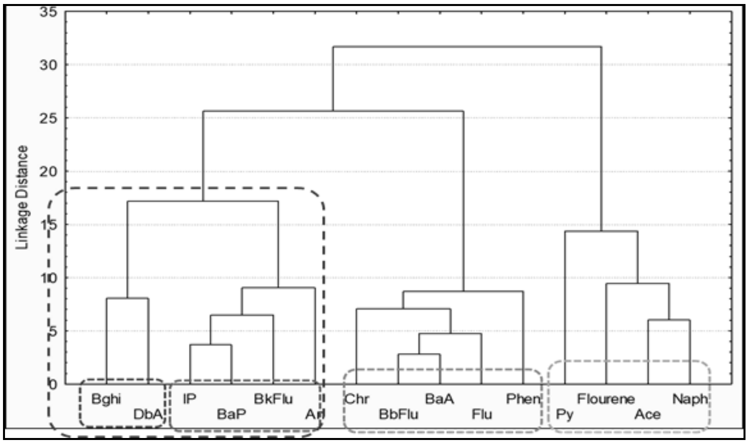

Fig. 1. The results of a cluster analysis of the distribution of PAHs in 142 natural and technogenic objects of various genesis

The distribution of 142 objects on the dendrogram obtained by cluster analysis based on data on concentrations of 15 PAHs is determined by the origin of contamination and the type of objects. There are 2 classes with markedly different values of average ΣPAH (ng/g): 1. Clean and relatively unpolluted environments (ΣPAH 226) and 2. Polluted environments (ΣPAH 3384).

By further iterations, the first class is subdivided into 1.1. Clean (ΣPAH 90.1) and 1.2. Having a tendency to pollution (ΣPAH 810). Further subclasses were divided into smaller groups: from 1.1.1. Clean for these formations (ΣPAH 106.0) to 1.1.1.2.4. Maximum clean (snow outside the pollution zone, ΣPAH 0.47); from 1.2.1. Relatively polluted (ΣPAH 632) to 1.2.2. With severe pollution (ΣPAH 1088).

The second class of contaminated media is divided into: 2.1. With severe pollution (ΣPAH 2430), including 2.1.1 with pronounced pollution (ΣPAH 2564) and 2.1.2 slightly contaminated (ΣPAH 1552) and 2.2. Very polluted (ΣPAH 3384), consisting of 2.2.1. Extremely polluted (ΣPAH 697) and 2.2.2. Very dirty (ΣPAH 5763).

Also, the media with abnormally high Σ PAU = 31,450 μg / kg – soil in the industrial zone of the Bratsk aluminium smelter were identified [8].

The dominant PAHs for all pure formations are Py, Naph, Phen, and Flu. In this pool, PAHs can change their places depending on the prevailing media in the clusters, the role and conditions regarding the press of pollution, as well as the degree of transformation in natural conditions and the influence of other media.

Analysis of specificity of PAHs distribution in the environmental media allowed us to identify some paradox moments.

1. Naph is considered as extremely unstable PAH having naphthidogenic nature, relatively soluble in water. Nevertheless, it is quite firmly fixed in plant communities, rhizosphere, soils, peat, tow. Apparently, this is due to the migration of moisture, permeating the entire cycle of plant development. According to the frequency of occurrence in environments, Naph is the leader (except for snow in the zones of influence of vehicles - it is absent there, due to the high temperature of fuel combustion in engines [9]). Similarly, Naph Phen and Flu are detected, although they are more resistant to environmental influences, and their appearance, in addition to pyrogenic technogenesis, may be due to the generation of organic matter.

2. Extremely low concentrations of PAHs in snow and water, despite the potential for accumulation. Low PAH concentrations in snow are regulated by the time of contact with precipitation. In the rivers most of the PAHs may migrate to the organic suspensions.

Therefore, measurements of their concentrations in water record only the dissolved part of PAHs. In underground waters, PAH concentrations are insignificant due to their vertical migration through rocks (except for hydrocarbon deposits). From the standpoint of thermodynamics, the water-rock interaction can be interpreted as a super-flow system, where the principle is implemented: the more matter and energy entered the system from an external source, the more significant amounts of them are converted with minimal synergetic processes [1].

3. The variety of time intervals during which the maximum accumulation of PAHs is achieved, and the synergy of factors for the formation of the PAH gradient in the media chain. Concentration occurs to a greater extent due to microeffects in each of the media with a relative constancy of macro factors (gravity, etc.). Concentration decreases in the sequence: the needles of cedar, larch, pine, the soil in the influence zone of aluminum production > drains below the ash dump TPP > soil, bottom sediments in the area of impact of the leather industry>soil and sediment in the impact zone exits of underground waters (Crimea) > soils, silts, peat, hards > needles, hydrophytes groundwater sources, the roots of Salicornia, Arctic soil > roots of plants, soils, sludges, polluted snow > water underground springs and mud volcano, surface water, clean soil of Antarctica; snow in Moscow. This sequence indicates the possibility of maximum accumulation of PAHs from the atmosphere in the coniferous trees, even in short periods of time (larch periodically sheds needles). Soils have their own limits of PAH saturation, although their ability to "process" petroleum products is higher than that of other media. Like sediments (silts), they can deposit PAHs up to certain limits. The maximum deposition, in addition to lipophilicity, is controlled by the effective diameter of the mineral matrix. The rhizosphere is a specific subsystem that controls selective PAH inputs from soil to stems; this is a "filter" that regulates mini-mass flows in plants. The spectrum of dependencies of entropy averaged over clusters on the coefficients of PAH concentrations in the considered groups is shown (Fig. 2).

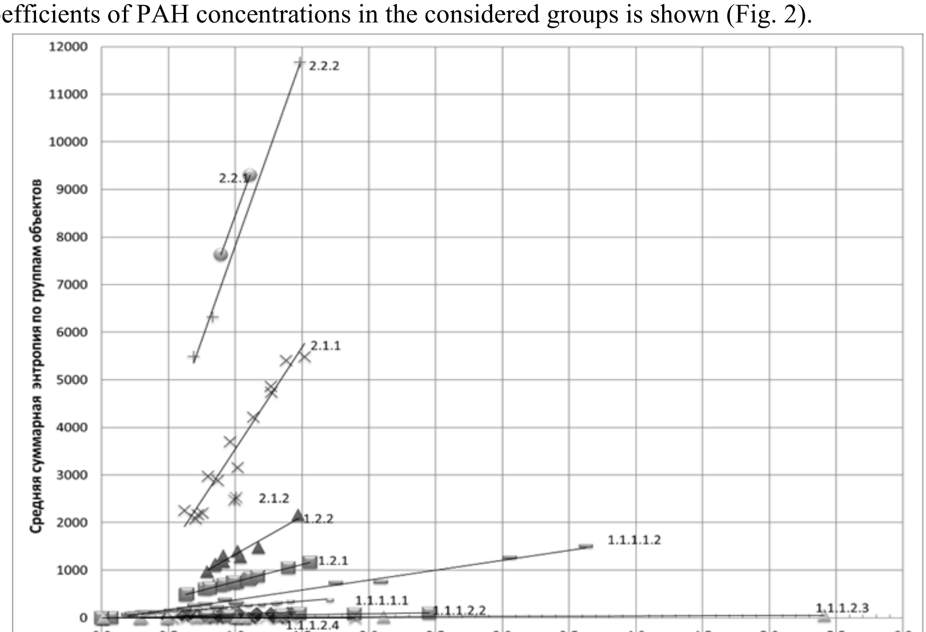

Fig. 2. The dependence of the total entropy on the CC for the selected groups of objects

A clear differentiation of points indicates the abrupt development of dissipative systems, with possible phase transitions at high entropy values. The separation of media with low entropy values and low concentration potential is unambiguous. These are polluted soil and rhizosphere of plants (industrial zone, drainage irrigation-cluster 2.2.1) and cluster 2.2.2 – larch needles from industrial areas of the Irkutsk region.

4. The fourth paradox is the role of biological systems for the transformation of PAHs. The underestimation of the role of living matter as a component of the geological environment (continuously and with minimal energy expenditures fulfilling the barrier role) leads to disruption of the functions of its components. For bottom sediments, it can be argued that they are approaching an altered stable asymptotic state, a weak reaction to external influences. Further, as the entropy decreases in clusters 2.1 1, 2.1.2, and 1.2.1, a regular increase in the concentration of PAHs in media occurs. These are mosses, lichens, rhizosphere, santolin wormwood, soil, and the most polluted bottom sediments of the river. Aojian, soil and plant rhizosphere in an irrigation experiment with industrial waste. For the first cluster, we can talk about the property of the plants themselves with maximum activity to absorb pollutants and natural PAH flows.

5. The fifth paradox: the generation and accumulation of PAHs, reaching maximum concentrations, can occur naturally through evolutionary catalysis. This path in open systems is anti-entropy in nature. Cluster 2.1.2. consists of 2 objects with a high PAH content due to natural concentration in the transitional and lower peat layers. High abilities are known for the generation and accumulation of hydrocarbons by this substance under favourable conditions. Given the close hydrocarbon composition of peat and oil products, these effects can be explained (except for self-generation) by the principle of "like tends to like". From the standpoint of nonequilibrium thermodynamics, the problem of assessing the stability of states as a measure of deviations from equilibrium under various external influences is of particular relevance. The state function of a system or its evolution can be identified based on the values of ΔS and ΔG. Based on empirical data, the values of standardized entropy for the selected clusters were calculated (Fig. 3).

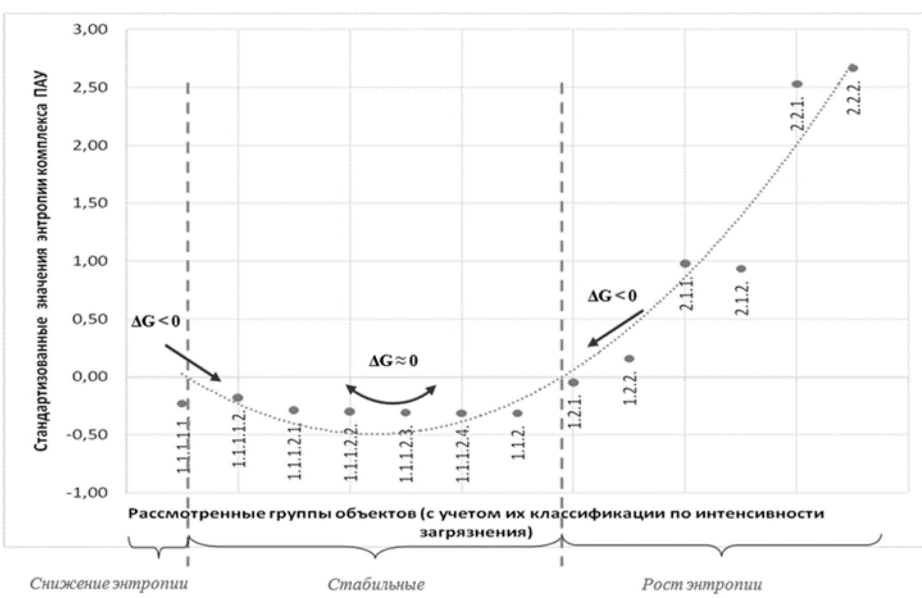

Fig. 3. Changes in the values of standardized entropy of ∑PAH in different genetic types of objects

6. The stability of GCS from the standpoint of thermodynamics is an equilibrium-nonequilibrium state; it is characterized by the centripetal directivity of the flows of matter and energy (Fig. 3).

The general dynamics of the variability of entropy depending on the properties of the media in which PAHs migrate is close to the theoretical model of the kinetics of transformation of the starting materials into reaction products. One can clearly see the tendency to minimize and go to the negative region of clusters from 1.2.1 to subcluster 1.1.1.1.1 (mainly taxa with a low level of PAH contamination in various environments). The values of thermodynamic parameters indicate that a conditional equilibrium is reached in the media when the influx of matter and energy into the system is approximately equal. Coordination of system elements creates an optimal margin of adaptation to external influences. Catabolic processes, biological (they are given the predominant role) and physicochemical (including the ablation of PAHs from a system with moisture streams) are active in all parts of the trophic chain of systems with a pulsed damped mode. This provides a time-delayed evolution of HCS or a steady development trend. Internal fluctuations of systems are balanced by external influences of the supersystem. PAH generation by the system itself is manifested by natural pools of fractions, and their local contribution is suppressed by the cumulative nature of the system itself. The second part of the curve with positive entropy values from the cluster 1.2.2. to the cluster 2.2.2. - heterogeneous systems with a pronounced technogenic influence. Here, PAHs are accumulating (to the maximum) with the participation of self-oscillating and autowave processes. Judging by the increase in energy parameters, the accumulation and destruction of PAHs are abrupt, and the formation of PAH pools at the output is stochastic.

7. The effects of concentration cannot be explained only by the kinetics of substances or their internal molecular properties. Mass flows in media are aimed at equalizing concentration gradients; these processes can be considered as the beginning of the fractionation of substances. They are selective depending on the physical properties of substances and purposefulness. For biota, an important role is played by the time intervals of "life" and the processes of fractionation are more contrasted. The osmotic properties of plants or porous media significantly reduce the role of thermodynamic forces. Mass flows tend to even out gradients and activate feedback between system components, giving an impetus to evolution. Low-gradient formations include clean and relatively unpolluted clusters 1.1.1.1 - 1.2.2; to highly gradient ones are polluted media, clusters 2.1.1 - 2.2.2, and media with abnormally high pollution (Table 1, Fig. 3).

Table 1. Estimates of the significance of thermodynamic parameters in the processes of fractionation and concentration of PAHs

Cluster of objects	Leading factors in the accumulation of PAHs
1.1.2 Aojian River polluted waters (influence of leather industry enterprises)	ΔS>lgKow>ΔHsolid>ΔG
1.2.1 *Technologically loaded :* soils and bottom sediments of the Aojian River	Extremely weak influence ΔS
1.2.2 *Technologically loaded:* plants in the Irkutsk region, relatively clean soil, p. Olha, runoff 2 km below the thermal power plant, Olha river bassin - soils	ΔHgas >ΔS
2.1.1 High PAH content: mosses, lichens, rhizosphere, santolin wormwood, soil, the most polluted bottom sediments of the Aojian River	lgKow>ΔG> ΔHsolid >ΔS> ΔHgas
2.1.2 High PAH content, natural objects - transitional and lower peat	Слабое влияние ΔHgas
2.2.1 *Contaminated soil and rhizosphere (industrial zone, runoff watering)*	No significant connection
2.2.2 *Industrial areas, larch (Irkutsk region)*	ΔHgas

1.1.1.1.1 Hydrophytes of Lake Chokrak and soleros; Arctic soil	ΔG>lgKow>ΔS> ΔHgas > ΔHsolid
1.1.1.1.2 Antarctica soil, Olha river - bottom sediments, silt of Lake Chokrak	ΔG>lgKow> ΔHgas >ΔS> ΔHsolid
1.1.1.2.1 Soils and plant roots in the aquatic system, silts of Lake Chokrak, clean soils of Antarctica	lgKow>ΔG>ΔS> ΔHgas > ΔHsolid
1.1.1.2.2 Water of the Olha River, clean soils of Antarctica, the root of an unpolluted soil system	ΔG ≈ lgKow ≈ ΔHsolid ≈ ΔS> ΔHgas
1.1.1.2.3 Chokrak lake water, soil and plant roots in the aquatic system of Chokrak lake, snow on the RUDN campus, clean soils of Antarctica	ΔG>lgKow> ΔHsolid >ΔS> ΔHgas
1.1.1.2.4 Snow, RUDN campus	No significant connections

For the considered groups, multiple correlations of physicochemical characteristics and PAH concentrations were calculated. The role of these characteristics was evaluated by the number of significant relationships. The host adopted a characteristic that gains most of the significant relationships (correlation coefficient of 0.5 or more). On this basis, “ratings” of the degree of influence of parameters on ∑PAH concentrations were formed (Table 1).

The calculation results indicate a predominant role in all media in the total concentrations of PAHs ΔG and log Kow. Entropy almost never takes the lead except for super-polluted waters in the effluents of the leather industry and technologically loaded soils at the aluminum plant.

In most pure formations, regardless of the genesis, the leading positions change between ΔG and log Kow, which may indicate the manifestation of local equilibrium in irreversible heterogeneous GHS, for example, in peat, needles of plants and some types of soils.

Conclusion

A huge role in the macrokinetics of phase transformations and, consequently, the concentration of migrating substances in nonequilibrium systems is played by aqueous solutions that introduce significant fluctuations in the energy field through the manifestation of mass transfer gradients.

Mass flows of substances in interacting media are aimed at equalizing gradients, reduce the role of thermodynamic forces in nonequilibrium systems. This leads to the formation of feedbacks in the system, according to the degree of influence of which the evolution (degree of self-organization) of the systems can be estimated.

The ratios of the concentration coefficients of PAHs in the media can be considered as the most informative parameter of the effectiveness of the nonequilibrium macro-system within the framework of the “input - transformation (or transformation) - removal of substances” scheme.

The minimum increment of entropy is formed in undisturbed media at the maximum contact of the supply vector and the minimum time intervals, which proves the relative stability of the flows.

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