

# Geochemical Markers Based on Concentration Ratios of PAH in Oils and Oil-Polluted Areas

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**Abstract**—The paper presents data on the possibility of using the proportions of concentrations of polycyclic aromatic hydrocarbons (PAH) as indicators of the pollution sources with oil hydrocarbons. Approaches are suggested to estimate the efficiency of these indicator ratios, and the efficiency of the currently used ratios is evaluated. Multivariate data analysis is applied to demonstrate how the ratios depend on the degree of transformation of the petroleum products. The data presented in the paper are utilized to more accurately determine the indicator ratios of oil-bearing samples with regard for the contamination age.

**Keywords:** polycyclic aromatic hydrocarbons (PAH), oil, petroleum products, contaminations, indicator ratios

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## INTRODUCTION

In 2001, the Stockholm Convention was signed on persistent organic pollutants (POP), and this convention was ratified by Russia ten years later. First the POP list comprised only the “dirty dozen” compounds and was later expanded to include 21 ones. Now more than 35 POP are analyzed in environments and regarded as supertoxicants. This group of compounds definitely includes certain polycyclic aromatic hydrocarbons (PAH), which are contained in crude oil (up to 4%) and its processing products.

World's leading countries achieved much progress in studying PAH in natural environments, industrial ejection and emissions, and in nutrients. Several of these compounds are subject of standardizing, their use is constrained, or they are withdrawn from circulation. Much attention is currently paid to the migration and transformations of these pollutants, because evidence was obtained that they are actively modified in geochemical processes and are able to form more toxic species when interacting with naturally occurring solutions. Russia has relatively little achieved in studying these problems over the past one and a half decades. The only PAH subject to obligatory monitoring in the country is benz(a)pyrene, for which MPC in air and water are standardized. The United States monitor 16 high-priority PAH listed by the Environmental Protection Agency, the European Union monitors four PAH, and China conducts studies of up to twenty compounds.

Although it was already V.I. Vernadsky who attached much importance to living matter and, hence, the organic component of geochemical systems, not much

is still done in studying interaction of living and “dead” matter. On the initiative of V.N. Florovskaya, M.A. Glazovskaya, N.P. Solntseva, A.A. Oborin, etc., Russia conducts studies of PAH migration and transformations in soils and biocenoses, including in polluted ones. Much less attention is paid to PAH pollution in surface and ground waters and in bottom sediments, and merely a few studies has so far been focused at these processes when mineral grounds are polluted.

Indicator PAH ratios are regarded as geochemical markers that make it possible to reliably identify the source of the pollution. Our research made use of extensive literature data on PAH contents in natural and anthropogenic objects and was aimed first of all on testing the adequacy of these estimates and the possibility of using the determined critical values of the indicator ratios at areas and facilities of the oil and gas complex in the country. Our results make it possible to select geochemical markers that are most sensitive to the character of pollution and that enable one to reasonably reliably infer PAH sources from the composition of the pollutant and the time of its emission.

## DISTINGUISHING FEATURES OF PAH AS GEOCHEMICAL MARKERS

The identification of the nature of pollutants (the sources from which PAH came and, hence, their concentrations in the oils and petroleum products) is complicated by the distribution of PAH, which can be synthesized in several natural and industrial processes.

In terms of their origin, all PAH can be provisionally classed into *pyrogenic* (i.e., formed by various

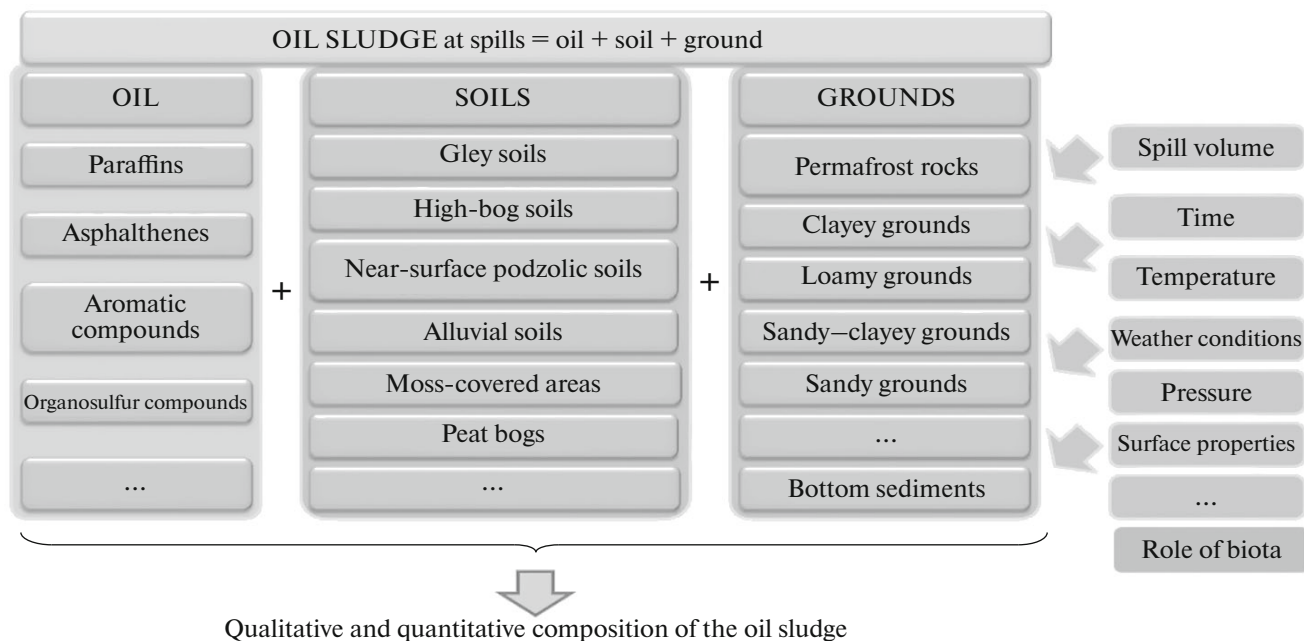


Fig. 1. Natural environments and factors of transformation of hydrocarbon pollution (Khaustov and Redina, 2014a).

burning processes, including combustion of domestic wastes) and *biogenic* and *petrogenic* (i.e., derived in any way from oil and not related to burning). Petrogenic PAH can also be produced by several geochemical processes involving hydrocarbons. The composition and structure of PAH and their stability depend on their genesis and on the temperature and geochemical environment into which they are brought.

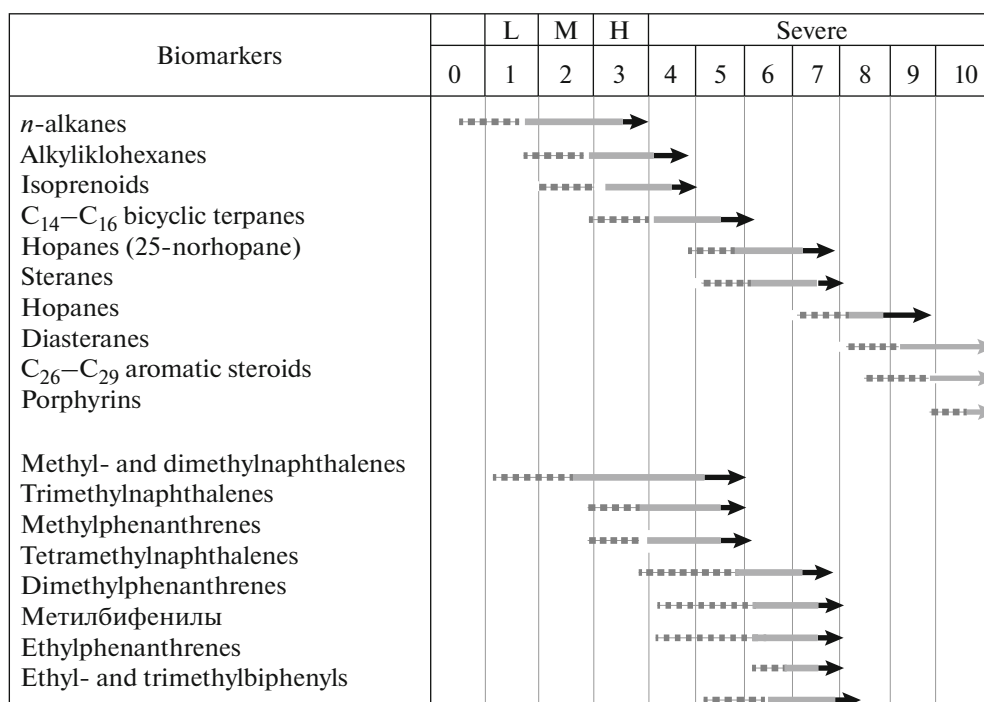
Underestimation of the role of PAH as supertoxic compounds (including PAH in areas polluted with oil and petroleum products) not only precludes selecting optimal technologies for the rehabilitation of the disturbed natural systems but also diminishes the efficiency of preventive environment-protecting measures. For example, more than a half of facilities for utilizing medical wastes was stopped in the United States in the late 1990s to study emissions of persistent organic pollutants (POP; first of all, PAH), which have been underestimated before.

Our earlier publications presented reviews of studies of the transformations of crude oil and petroleum products in environment (Khaustov and Redina, 2012, 2013, 2014b). Although PAH belong to POP, several researchers have proved that some PAH can be actively transformed and are able to migrate in nature for significant distances. Oil and petroleum products pollutions can be transformed under the effect of several factors. As an example, this can be illustrated by Fig. 1 for oil sludges, which are formed at oil spills.

The transformations rates and pathways of PAH are highly diverse. For example, some PAH can be preserved in soils for hundreds of years depending on their geochemical stability. This is largely explained by

the chemical composition of PAH and their decomposition kinetics. Pyrogenic PAH show strong affinity to volatile organic particles (soot and biogenic suspensions), which can be transported for significant distances with wind and other atmospheric agents. Much PAH can be transported with mechanical and organic suspensions in water currents and can be coprecipitated with bottom sediments (Nemirovskaya, 2008). Heavy and complicated compounds of crude oil and petroleum products are relatively more resistant to degradation, including microbial one. The following degradation successions are reported in (Asif, 2010). The first PAH to be decomposed are those with a small number of benzene rings. Alkylated PAH are characterized by varying degradation capability (including microbial one) depending on the number and length of their alkyl groups. The degradation rates and sequences of *n*-alkanes are illustrated in Fig. 2 in comparison with those of aromatic compounds.

All compounds of oils are thus subject of transformations, but the decomposition sequences of these compounds are controlled by the complexity of their molecules (or the numbers of benzene rings in the aromatic compounds) and by the numbers of alkyl groups (if present). Degradation modifies the composition of oil pollutions. Knowing the degradation rates and original composition of a pollution, one can predict the evolution of the pollutants. At the same time, data on modern pollutions can be utilized to estimate the original composition of the oil and petroleum products and thus identify their source. In the latter instance, the researcher faces certain difficulties stemming from the fact that the oil composition may be similar to that of



**Fig. 2.** Biodegradation sequence of aliphatic and aromatic compounds in crude oil. Arrows indicate the decomposition of classes of compounds, dashed lines show changes in compounds, the gray solid line corresponds to significant depletion, the black solid line corresponds to complete decomposition. The evolution of the biodegradation process modifies the quality of the oil: L—light, M—medium, H—high, Severe—severe modifications (Asif, 2010).

unpolluted natural materials, for example, peat. Geochemical similarities between oil and peat in terms of composition of all major hydrocarbon groups (unsubstituted HC and heterocompounds) are convincingly demonstrated in (Bachurin and Odintsova, 2005). This situation calls for using more sensitive indicators of the provenance of petroleum products in polluted environments. As a possible solution of this problem, below we suggest various coefficients that should be indicative of the origin of the pollution. These approaches are underlain by understanding the stability of these compounds.

Structures with angular successions, with an angular arrangement of the benzene rings (phenanthrene) are more stable, whereas linear chains and alkylated homologues are less stable. The former are ascribed to thermodynamic isomers, and the latter are referred to kinetic ones. Intensification of industrial anthropogenic activity disturbs the natural tendency toward an increase in the percentage of thermodynamic groups, and kinetic isomers become dominant because of the shorter times of their transport and differentiation in soil-forming and sedimentary processes. The composition of PAH can remarkably vary depending on their genesis: petrogenic, pyrogenic, or biogenic. The compounds of the first group are mostly pyrenes and benzopyrenes, and the latter are phenanthrenes.

Biogenic PAH are usually generated during early diagenesis due to biochemical and microbiological transformations of organic compounds of dominantly

humic nature. Typical compounds of this group are phenanthrenes, chrysenes, and perylenes.

Below we discuss the informativeness of the suggested indicators of PAH genesis.

## METHODS

Approaches to determining the genesis of PAH (Rovinskii et al., 1988; Khaustov and Redina, 2012, 2014a; Inengite et al., 2012; Țigănuș et al., 2010; Sakari, 2012; Soclo et al., 2000; Yunker et al., 2002) are generally based on using the following indicators and methods:

- proportions of alkyl-substituted and original PAH;
- proportions of instable “kinetic” PAH (such as fluoranthene, which possesses a ring of five atoms) and more stable “thermodynamic” PAH (for example, pyrene, whose ring consists of six atoms), which may be indicative that PAH were synthesized by burning (and hence, suggest an anthropogenic source of the pollution);
- possible origin of PAH from a certain source; for example, acenaphthene and acenaphthylene are typical of burning products, while cadalene and retene are typically found in plant-derived materials;
- application of statistical identification techniques if all of the aforementioned estimates are links of a single calculation routine; the variations in the

concentrations (proportions) are utilized to differentiate between various hydrocarbon groups and within these groups.

Currently most popular (both in Russia and abroad, for example, in the United States, Canada, China, Taiwan, etc.) techniques make use of indicator PAH ratios. Their application is made possible by knowing the degradation rates of PAH, with the dominance of certain isomers in various anthropogenic processes (for example, three PAH compounds possess equal molecular weight of 228: triphenylene, chrysene and benzanthracene; and seven PAH isomers have a molecular weight of 252), or with regard for transformations of original PAH into certain products (alkyl- and halide-substituted species). PAH isomers differ in heat of formation and, correspondingly, reacting capability. The “kinetic” (less stable) isomers are understood as those whose heat of formation is greater, whereas “thermodynamic” isomers are more stable, and their heat of formation is minimal. For example, anthracene is the kinetic and is phenanthrene the thermodynamic isomer in the phenanthrene–anthracene pair, and fluoranthene is the kinetic isomer and pyrene is the thermodynamic one in the pyrene–fluoranthene pair, etc. Certain PAH sources typically contain certain isomers, and variations in the ratios with time can be used to evaluate the age of the object.

The most widely used PAH indicator ratios are those calculated for compounds of the same molecular weight (isomers), with some of which regarded as “kinetic” and others as “thermodynamic” (more stable) ones. Table 1 lists the most commonly utilized indicator ratios and recommended threshold values for identification of PAH genesis.

In analyzing the transformation rates of various PAH, one should take into account the thermodynamic stability of the original PAH and also to know characteristics of various PAH sources, how the PAH composition varies when the compounds are transferred from the source to the “recipient” environments, and the relative stability of various PAH isomers. For example, data obtained by foreign researchers cannot be directly translated to situations in Russia because of differences in the natural environments, including seasonal conditions. Furthermore, it is widely known that the stability sequences of various PAH in winter and summer differ depending on sunlight intensity, temperature, and humidity (Rovinskii et al., 1988; Inengite et al., 2012; and others).

As was mentioned above, such estimates are not always unambiguous, and the threshold values of the indicator ratios may require revisions with reference to certain instances. This is illustrated below by the example of estimating the informativeness of the coefficients utilized at oil pollutions (based on data of Russian and foreign researchers).

## RESULTS AND DISCUSSION

Consider the possibility of identification of the sources of pollution of obviously oil-related (petrogenic) nature. We have searched the literature for oil-bearing samples of various nature: sampling region, exposure time at the surface, etc. The analyses show that certain PAH are highly variable, which allowed us to examine the whole possible ranges of their transformations in various environments and the variations in the errors related to using various extraction and analytical techniques (which accounts for the possible “noisiness” of the statistical data on our selection of samples). At the same time, the broad variations of the data allowed us to demonstrate the necessity for conducting specialized calculations to warrant the selection of the PAH indicator ratios.

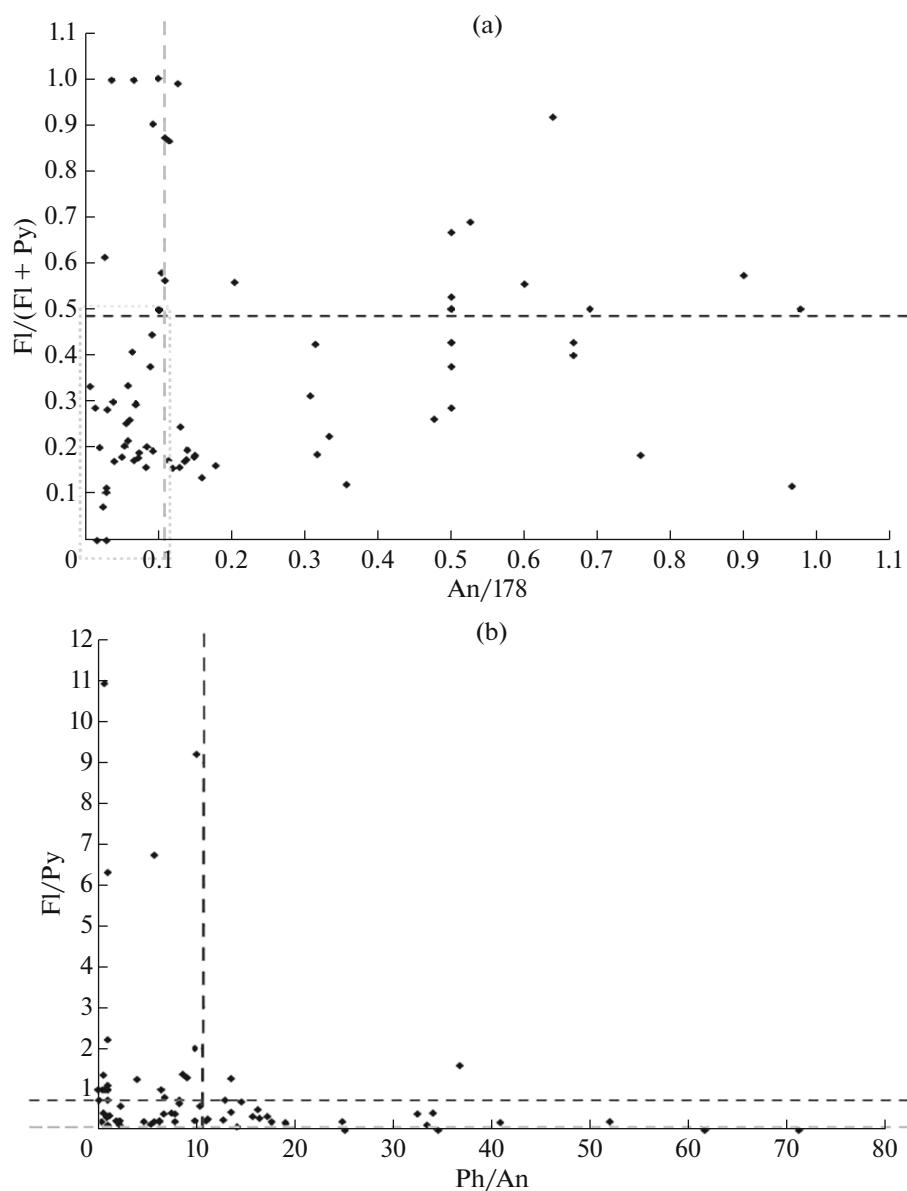
Our calculations were conducted using the following input data: (a) data on averaged oil samples from the West Siberian and Volga–Ural hydrocarbon provinces according to (Ozhegov et al., 2014), with oils from these fields brought to oil refineries upon preparatory processing at the fields and transported via pipelines; (b) data on samples from sludge pits at abandoned exploration wells drilled at the Uvatskaya group of hydrocarbon fields in the Khanty–Mancy Autonomous Territory (KMAT), according to data in (Soromotin et al., 2010); PAH concentrations in a reference soil sample, mix of the crude oil and soil (sampled at depths of 0–7 and 7–10 cm), and oil sludge samples (from depths of 0–3 and 3–30 cm); (c) data on PAH distribution in the vertical sections of soils polluted with the Usinsk oil (in the Komi Republic) according to (Anchugova et al., 2010); (d) data on PAH contents in bottom sediments from an OD storage reservoir in the United States (Kerr et al., 1999); (e) data on PAH concentrations in oil-polluted soils in the United States (Pampanin et al., 2013) and data on PAH concentrations in an averaged sample of 48 various oils from United States (Pampanin et al., 2013); (f) PAH concentrations in oils from fields in the North Sea (Pampanin et al., 2013); (g) PAH concentrations in dry and fresh oil sludge from the Zhongyuan field in China (Kuang and Zhao, 2011); (h) data on PAH degradation as a result of photolysis of naturally occurring bitumen in Nigeria (four samples, samples exposed to solar radiation for 0, 1, 3, and 6 months) according to (Olabemiwo et al.); and PAH concentrations in soils within the influence zone of an oil refinery (Inengite, 2012); (i) PAH concentration in geothermal crude oil samples (Kawka, 1990), data on PAH concentrations in sludge from a flocculation–flotation facilities at an oil refinery in the United States (Kriipsalu et al., 2008), and data on PAH degradation (Ubani, 2012) in the presence of biological fertilizers (composting); and (j) data on PAH concentrations in bitumen utilized at oil refineries for producing asphalt (Bowen, 2000).

**Table 1.** Indicators of PAH nature for various environments (Rovinskii et al., 1988; Țigănuș et al., 2010; Sakari, 2012; Soclo et al., 2000; Yunker et al., 2002)

Values for petrogenic PAH	Values for pyrogenic PAH
1	2
Phenanthrene/anthracene (Ph/An)	
Ph/An > 10.0	Ph/An < 10.0 Ph/A ≈ 3.0 at wood and coal burning
Anthracene/(sum of isomers of atomic weight of 178), An/(Ph + An) or An/178	
An/(Ph + An) > 0.10 ⇒ diesel oil, shale oil, coal, and some crude oil samples	An/(Ph + An) < 0.10 ⇒ lignite and emissions of diesel fuel and oil pitch
Fluoranthene/pyrene, Fl/Py	
Fl/Py > 1.0 [13] Fl/Py < 0.4 [10–12]	*Fl/Py < 1 ⇒ pyrogenic sources; • Fl/Py < 1.4 coal burning; • Fl/Py < 1.0 wood burning □ Fl/Py > 0.4 burning
Fluoranthene/(fluoranthene + pyrene), Fl/(Fl + Py)	
Fl/(Fl + Py) < 0.50 ⇒ most OD and oil burning products	Fl/(Fl + Py) > 0.50 ⇒ burning kerosene, grass, most coal types, wood, and creosote
Benz(a)anthracene/(benz(a)anthracene + chrysene (triphenylene)), BaA/228	
BaA/228 < 0.20	BaA/228 > 0.50 PAH – burning product BaA/228 > 0.35
Indene(1,2,3-cd)pyrene/indene(1,2,3-cd)pyrene + benz(ghi)perylene, IP/(IP + Bghi)	
IP/(IP + Bghi) < ≈0.20	• IP/IP + Bghi > 0.5 burning grass, wood soot, wood, and coal; bush fires, • IP/IP + Bghi < 0.5 savannah fires; OD and crude oil burning products
(Pyrene + fluoranthene)/(chrysene + phenanthrene) (Py + Fl)/(Chr + Ph)	
<0.5	>0.5
Concentration ratios of low- (LM) and high-molecular weigh (HM) PAH	
LM/HM > 1.0	LM/HM < 1.0
Methylphenanthrene and phenanthrene (MP/P)	
MP/P > 4.0—engine oils	• ≈ 1.0 for street and urban dust samples; • 2.0 ... 6.0 burning fossil fuel (direct injection technology)
(Methylfluorantehne + methylpyrene)/fluoranthene (MFl + MPy)/Fl	
(MFl + MPy)/Fl > 1	(MFl + MPy)/Fl < 1

Obviously, there cannot be any two fields whose oil compositions are exactly identical. Moreover, PAH concentrations vary even in a single well with time. None of the aforementioned sources was related to oil burning, and hence, we assumed that the indicator ratios should generally lie (with certain differences) within the conventionally adopted ranges of threshold values. However, our calculations show that far from all of the coefficients are informative: some of them do not unambiguously point to a petrogenic nature of the pollutants. Figures 3a and 3b show the arrangement of the data points of the samples relative to the axes that

correspond to the most widely utilized indicator ratios. The figures obviously demonstrate the different (and, unfortunately, not high) informativeness of the currently conventionally utilized PAH ratios. Even the ratios involving fluoranthene and pyrene concentrations, which are commonly thought to be reliable indicators of an oil provenance of PAH, turned out to be informative in far from all of the instances. For example, Fig. 3a shows that three-fourths of the samples do fall within the threshold ranges, while the “oil” range in Fig. 3b according to the criterion Fl/Py < 0.4 includes only as few as roughly half of the samples.



**Fig. 3.** Distribution of objects in the planes of PAH indicator ratios: (a)  $FI/(FI + Py)$  and  $An/(Ph + An)$ ; (b)  $FI/Py$  and  $Ph/An$ . The dotted line contours values recommended as thresholds for indicator ratios of samples of oil nature.

The informativeness of these indicator PAH ratios is thus different (Table 2), with the percentage of identifications falling within the ranges specified in Table 1 varying from 20.8 to 79.2. The maximally accurate estimates of PAH genesis for petrogenic sources are yielded by the ratios  $FI/(FI + Py) < 0.50$  (76.6% accurate estimates) and  $An/(Ph + An) > 0.10$  (57.1% accurate estimates), and the minimum accuracy was shown by the indicator ratio  $(Py + FI)/(Chr + Ph) > 0.5$ .

In our opinion, the inaccuracies of the estimates stem first and foremost from the diversity of the transformation conditions of the original PAH in various natural environments (KMAT, North Sea, Komi Republic, and various natural zones in the United

States and Africa). The composition of the pollutions also remarkably varies. Furthermore, a certain role could be played by the differences in the exposure time of the oils on the surface (with these times different for the oil sludges and crude oils), and for the oil sludges, also contact with the compounds utilized when wells are drilled. Obviously, oil processing technologies at refineries should also have affected the composition of the samples (one of them was from flocculation–flotation facilities). A good example of the effect of the natural environmental conditions is presented in (Kriipsalu et al., 2008) for the dry and rainy seasons. These authors convincingly demonstrate that the oil-polluted soils show variations not only in the total

**Table 2.** Estimated efficiency of PAH indicator ratios\*

Indicator ratio	Number of accurate identification (per 77 measurements)	Accurate identifications, %
Ph/An > 10	30	39.0%
Fl/Py > 1	23	29.9%
Fl/Py < 0.4	40	52.0%
An/(Ph + An) > 0.10	44	57.1%
<b>Fl/(Fl + Py) &lt; 0.50</b>	59	76.6%
<b>BaA/228 &lt; 0.20</b>	38	49.4%
<b>IP/(IP + Bghi) &lt; 0.20</b>	28	36.4%
(Py + Fl)/(Chr + Ph) > 0.5	15	19.5%

\* The most “efficient” indicator ratios are printed in bold face.

PAH concentrations but also in their proportions: the Fl/Py ratios during rainy and dry seasons vary by factors of 1.2–2.

To statistically estimate the dispersion of the data, we have conducted component analysis of a database on 77 objects (samples) and seven coefficients (indicator ratios) of PAH reported in Table 3. The method of principal components (MPC) is widely applied to study the reduction of an attribute space and identify a few principal vectors (principal components or PC) that mostly “accumulate” the dispersion of the attributes. This procedure enables one to get rid of less important variables and consider the objects from the standpoint of their distribution relative to the recognized PC. A MPC-based systematics of objects enable one to conduct unbiased recognition of groups based on a complex of attributes (features).

The calculations were carried out with the STATISTICA 7.0 program package (MPC, rotation of axes—Varimax normalized method). As a result, we distinguished three PC that account for 63% of the overall dispersion of the attributes, which are interpreted as follows (Table 3).

PC<sub>1</sub> (27% dispersion) comprises the indexes (ratios) Ph/An and An/(Ph + An), whose contributions to PC<sub>1</sub> are statistically significant (with opposite signs), and also IP/(IP + Bghi). This “architecture” of the component may be explained by the calculation technology of the indicator ratios. PC<sub>2</sub> (19% dispersion) encompasses the Fl/Py and Fl/(Fl + Py) ratios, whose values are high. These indexes make it possible to relatively efficiently identify an oil-related nature of PAH, and the percentage of PC<sub>2</sub> is practically the same as that of the explained dispersion of PC<sub>3</sub>. PC<sub>3</sub> (18% dispersion) involves the indicator ratio BaA/(BaA + Chr), whose contribution is relatively high.

The (Py + Fl)/(Chr + Ph) ratio is not included in any PC with a significant contribution, which led us to believe that this ratio is little informative for our selection of data.

The distribution of the data points (77 samples) in the PC<sub>1</sub> and PC<sub>2</sub> plane shows a relatively homogeneous grouping of the points along the axis PC<sub>1</sub>, although the contribution of this component to the overall dispersion of the attributes is relatively low. The likely anomalies are the Usinsk crude oil from the depth range of 7–30 cm, which is explained by the very low pyrene concentration in the sample, and oils from fields in the North Sea, which contain elevated phenanthrene concentrations.

Groups of objects are more contrastingly distinguished in the PC<sub>2</sub> and PC<sub>3</sub> plane (Fig. 4). A number of data points plot far away from the recognized groups. These points correspond to samples characterized by the most significant transformations in nature (decomposition under sunlight for 1 and 6 months), samples of oil-polluted soils, and a consolidated sample of 48 various oils. It is interesting that the samples of oils, oil-polluted soils, and sludge from the bottom of the sludge pit in the United States plot in the top left-hand quadrant of the diagram, while the samples of Nigerian bitumen and sludge from the pit of a well at the Uvatskaya group of fields in KMAT plot in the top right-hand quadrant. A possible explanation of this is

**Table 3.** Factor loads for PC<sub>1</sub>–PC<sub>3</sub>\*

Indicator ratio	PC <sub>1</sub>	PC <sub>2</sub>	PC <sub>3</sub>
Ph/An	<b>−0.75</b>	−0.16	0.32
Fl/Py	−0.17	<b>0.87</b>	−0.14
An/(Ph + An)	<b>0.82</b>	0.01	0.00
Fl/(Fl + Py)	0.31	<b>0.71</b>	0.35
(Py + Fl)/(Chr + Ph)	−0.02	0.01	0.45
BaA/228	0.04	0.05	<b>0.86</b>
IP/(IP + Bghi)	<b>0.72</b>	−0.12	0.26
Expl.Var	1.87	1.31	1.25
Prp.Totl	0.27	0.19	0.18

\* Statistically significant loads are printed in bold face.

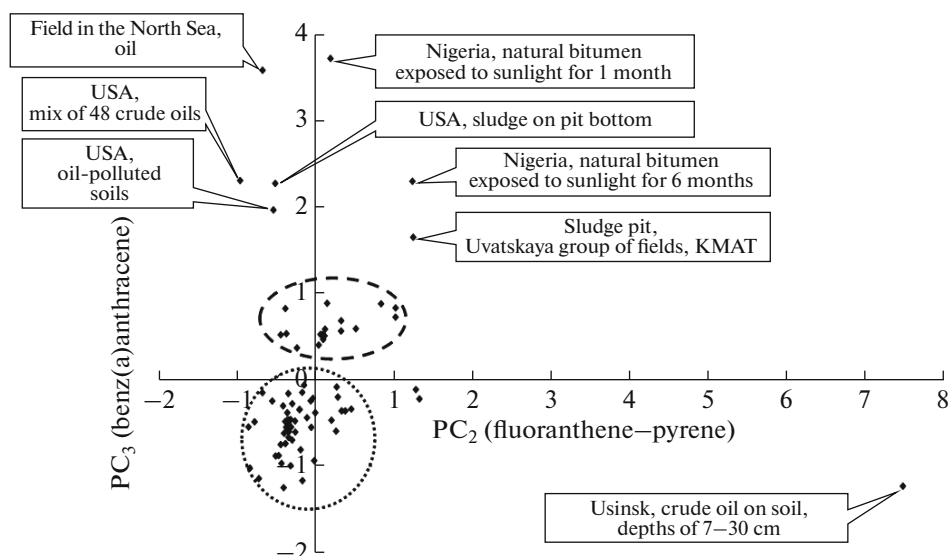


Fig. 4. Distribution of objects in the plane of PC<sub>2</sub> and PC<sub>3</sub>.

the regional compositional specifics of the oils and bitumen or the specifics of the sampling and extraction procedures.

The upper group of data points (group 1) pertains to samples from upper soil layers polluted with oil sludge (Usinsk), pure soils in the area of the experiment with Usinsk oil, soil samples in the influence zone of an oil refinery in Nigeria (the samples were collected mostly during the rainy season), a sample of Nigerian natural bitumen exposed to sunlight for 3 months, oil sludge samples subjected to composting in the presence of animal manure for 10 months, dry and fresh boring mud from China, and two oil samples from Venezuela. It is thus possible to reliably interpret this group as comprising samples containing deeply transformed PAH.

The lower group (group 2) is made up of most samples from sludge pits at wells in the Uvatskaya group of fields in KMAT, soil samples in the influence zone of an oil refinery in Nigeria (collected during the dry season), a sample of natural bitumen not affected by photolysis from Nigeria, all samples of hydrothermal oils, an averaged sample of 60 oils collected worldwide, five of the seven samples of Venezuelan oils, boring mud from Nigeria, bitumen used to produce asphalt (so-called standard Near East bitumen and that obtained via superfast vacuum refining), and sludge from flocculation-flotation facilities at an oil refinery in the United States. The samples thus correspond to insignificantly transformed compositions. The fact that the group includes sludges from pits at the abandoned wells at the Uvatskaya group may be explained by the relatively low rates of natural degradation processes of oil compounds.

This group displays obvious distinguishing values of the indicator ratios (Table 4). For instance, possess-

ing relatively closely similar values of certain indicator ratios (such as Ph/An and (Py + Fl)/(Chr + Ph)), the two groups show obvious differences in others. For example, the Fl/Py ratios of the groups are more than fivefold different, the BaA/(BaA + Chr) ratios are different by a factor of 2.5, and the An/(An + Ph) and IP/(IP + Bghi) ratios are roughly 1.5 times different. Comparison of the indicator ratios of the two groups with the values conventionally assumed for oil samples (Table 1) show fairly significant deviations of certain coefficients. Obviously, the ranges of the indicator ratios should be specified for each individual object.

These examples demonstrate serious problems in unambiguous distinguishing oil-polluted samples with different degrees of transformations of the original PAH compounds. Statistical analysis reveals significant differences between the storage parameters of the sludges, the composition of the original crude oils and bitumen, the effect of the exposure time to the environment, and the effects of climate and regional specifics of the samples. All these factors are responsible for the different dispersions of the PAH ratios typical of the samples.

Summarizing the aforesaid, we suggest a theoretical model for PAH-based genetic estimates for multi-component environments. The model is based on proportions of kinetic and thermodynamic isomers whose molecular weights are 178, 202, 228, and 252.

$$K_{\text{complex PAH}} = \left[ \frac{\text{An}}{\text{Ph}} + \frac{\text{Fl}}{\text{Py}} + \frac{\text{BaA}}{\text{Chr}} + \left( \frac{\text{BaP}}{\text{BeP}} + \frac{\text{BbF}}{\text{BeP}} + \frac{\text{BkP}}{\text{BeP}} \right) + \left( \frac{\text{IP}}{\text{Bghi}} + \frac{\text{DbA}}{\text{Bghi}} \right) \right]. \quad (1)$$

In a simplified form, this model can be realized as a coefficient that is a sum of the most widely utilized



**Table 4.** Indicator ratios of two groups of oil-bearing samples \*

Statistical characteristics of groups	Indicator ratio						
	Ph/ An	Fl/ Py	An/ (Ph + An)	Fl/ (Fl + Py)	(Py + Fl)/ (Chr + Ph)	BaA/ (BaA + Chr)	IP/ (IP + Bghi)
	Group 1						
Minimum	0.02	0.22	0.01	0.18	0.26	0.40	0.00
Maximum	71.11	9.21	0.98	0.90	4.72	0.71	1.00
Average	10.08	<b>2.14</b>	<b>0.38</b>	<b>0.54</b>	1.46	<b>0.48</b>	<b>0.63</b>
	Group 2						
Minimum	0.04	0.00	0.02	0.00	0.21	0.00	0.00
Maximum	61.54	303.03	0.97	1.00	7.88	0.44	1.00
Average	12.16	<b>11.27</b>	<b>0.21</b>	<b>0.29</b>	1.25	<b>0.19</b>	<b>0.37</b>
Values of indicator ratios conventionally assumed for PAH of petrogenic nature							
Ranges of indicator ratios	>10	>1** <0.4***	>0.10	<0.50	<0.5	<0.20	<0.20

\* Significantly different values are printed in bold face.

\*\* According to (Yunker et al., 2002).

\*\*\* According to (Soclo et al., 2000; Sakari, 2012; and others).

ratios of the concentrations of kinetic and thermodynamic PAH isomers

$$K_{\text{PAH}} = \text{An/Ph} + \text{Fl/Py} + \text{BaA/Chr} + \text{Ip/Bghi}. \quad (2)$$

Our calculations for the selection of data yielded high correlation coefficients (0.99) for the coefficient  $K_{\text{PAH}}$  and the Fl/Py ratio, and this allowed us to specify the threshold values for this coefficient. Comparison with these values shall provide information on the degree of transformations of the oils and petroleum products in the sampled materials. This value is 4 for samples proved to contain the most significantly transformed compounds and 13 for less strongly transformed ones. Note that the structure of the correlations between the indicator ratios of PAH may be different for other environments.

The behavior of certain PAH isomers depends on certain characteristics of the environments in which these compounds undergo transformations and on the nature of the sources in which they were generated. For example, benz(a)pyrene, which is traditionally studied in this context in Russia (because of the history of the studies and the availability of pertinent standards for certain environments) is a low-solubility compound and, hence, is indifferent to water. It can be easily and strongly adsorbed on mechanical suspensions of particles of small diameter and even be more strongly adsorbed on organic suspensions. Because of this and in spite of their kinetic nature, its ratios are little informative for both genetic estimates and those of the degrees of PAH transformations in various environments. At the same time, the toxicity of other isomers and the overall hydrocarbon contamination are estimated related to this isomer, although it can be generated by natural processes.

## CONCLUSIONS

1. Application of PAH indicator ratios makes it possible to obtain variably reliable estimates for the genesis of these PAH of oils and oil sludges. The maximally accurate differentiation between petrogenic and pyrogenic PAH is achieved by using the Fl/(Fl + Py) ratio, i.e., that of PAH whose molecular weights are 202.
2. The threshold values of the indicator ratios that are widely utilized in the foreign literature cannot be automatically translated to all possible conditions and environment types but should be significantly revised and corrected, with the justification of their application depending on the materials to be examined, their storage time, and the extraction techniques.
3. In view of the significant variations in PAH concentrations and the probability that various analytical techniques are used, the physicochemical analyses should be replicated, standard reference samples should be utilized, and the techniques of PAH extraction should be specified.
4. The application of a complex of ratios indicating the genesis of PAH and the use of techniques of statistical multidimensional analysis make it possible to less ambiguously distinguish between oil-bearing samples of various nature, which are different in composition and were exposed on the surface during different time spans. This also enables the researcher to relatively reliably identify samples that suffered transformations of different degree.
5. Conditions on the Earth's surface significantly imprint the composition and proportions of PAH. Transformations of petroleum products on the surface and their migration with certain components of an environment modifies PAH proportions compared to those of the original "fresh" oils and pollutions. This is also

reflected in the indicator ratios and provides a possibility of distinguishing between pollutions of different age.

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