Inna A. Nemirovskaya
P.P. Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, Russia
e-mail: nemir@ocean.ru

DISTRIBUTION OF HYDROCARBONS IN PARTICULATE MATTER AND BOTTOM SEDIMENTS OF THE VOLGA DELTA

ABSTRACT

Data are presented on the content and composition of hydrocarbons (aliphatic and polyaromatic) in the filtered particulate matter and in the surface layer of the bottom sediments of the Volga River and the northern shelf of the Caspian Sea. Because of transformation and precipitation of anthropogenic and natural compounds, the HC composition in particulate matter and bottom sediments undergoes changes caused by precipitation of particulate matter, varying temperatures, and mixing of fresh and saline waters. It appeared that the greatest accumulation of the HC proceeds in the region of avalanche sedimentation, and their content is independent of the grain-size type of the sediments. The anthropogenic HC (oil and pyrogenous) do not pass the marginal filter of the Volga River and do not enter the open part of the sea.

KEY WORDS: geochemical barrier, marginal filters, oil, hydrocarbons, aliphatic hydrocarbons, alkane, polycyclic aromatic hydrocarbons, suspended particulate matter, bottom sediments

INTRODUCTION

The Caspian Sea is one of the richest oil-and-gas bearing regions with the hydrocarbon potential estimated at 16–32 billion barrels [Efimov, 2000]. Here, natural oil seepage can occur, as well as the entry of oil hydrocarbons (HC) with pollutants as a result of intense oil extraction and transportation of hydrocarbon fuel [Dumont, 1998]. The main pollution sources for the northern part of the Caspian Sea are the coastal oil production, navigation, and the Volga River runoff [Dumont, 1998; Tolosa et al, 2004]. The northern part of the Caspian Sea containing a little more than 1% of the water of the sea (because of the shallowness) receives about 90% of the total riverine runoff, and 80% of the biogenic organic matter (OM) is supplied by the Volga River runoff alone [Shiganova et al, 2003]. In the transformed Volga waters supplied from the avandelta, the content of dissolved C_{org} varies from 500 to 667 μM [Agatova et al, 2005].

According to the model proposed by Academician A.P. Lisitsyn, the area of riverine and marine water mixing (marginal filter [Lisitsyn, 1995]) consists of three basic zones with specific functions: gravitational, physicochemical, and biological. In the gravitational zone, because of the damming of riverine water by marine water, sedimentation of sand–silty fractions occurs; this area has high water turbidity and hindered photosynthesis. In the physicochemical zone, colloids and dissolved compounds are captured (the zone of flocculation and coagulation). After sedimentation of various compounds and water clearing, phytoplankton develops and the biological zone emerges (assimilation and transformation of dissolved substances of mineral and organic composition). The studies performed earlier in the coastal waters of the Caspian Sea showed that the sandy bottom sediments (2003, Fig. 1) had rather low concentrations of organic compounds and contained from 0.031 to 0.59% C_{org} and from 19.8 to 142.1 μg/g of

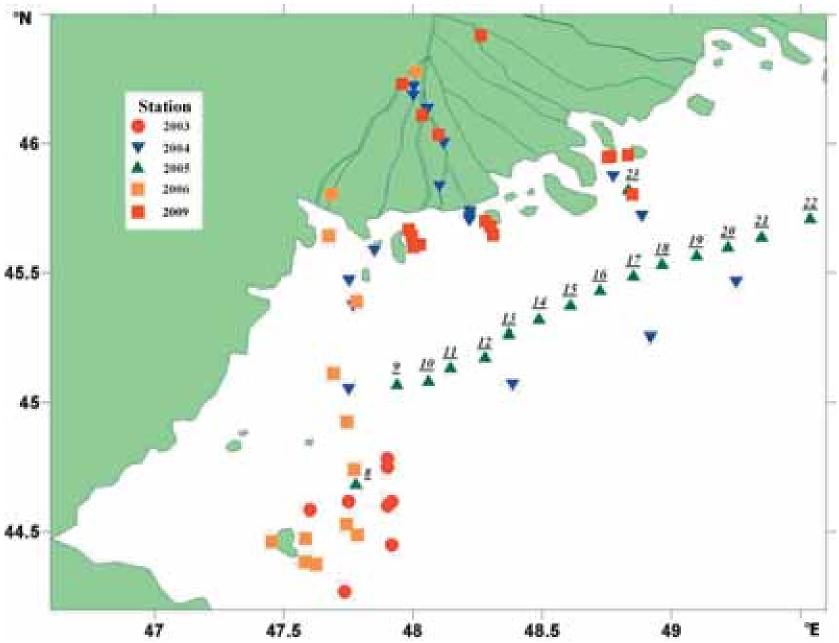

Fig. 1. The sampling scheme of the northern shelf of the Caspian Sea (2003–2009 – bottom sediments; 2006 – filtered particulate matter).

8–22 – station nos. where the bottom sediments were sampled in 2005

aliphatic hydrocarbons (AHC) [Nemirovskaya and Brekhovskikh, 2008]. A weak statistical correlation between the distribution of C_{org} and AHC (r = 0.14) indicated different origins of these compounds. On the contrary, the sediments sampled in 2004 in the channels of the Volga River (the gravitation part of the marginal filter) had high concentrations of both C_{org} (up to 8.6%) and AHC (up to 3881µg/g). The AHC fraction in the Volga River channels was, in several cases, as high as 16.8–23.9% of C_{org}, which was considerably higher than that in other aquatic areas with a permanent oil supply [Nemirovskaya, 2004; Tolosa et al, 2004].

In 2005, 2006, and 2009, the studies of the northern shelf of the Caspian Sea were continued and samples of particulate matter and bottom sediments were collected. In 2009, the studies of the Volga River (from Konakovo to channels of the Delta Volga) took place. These studies were aimed at identification of the genesis of AHC and polycyclic aromatic HC (PAH) and their transformation in the Volga Delta (Fig. 1).

Because of their hydrophobic properties, HC are easily sorbed by particulate matter and, during the sedimentation, fall to bottom sediments, which accumulate these compounds. Therefore, the processes of OM transfer and transformation may be identified through comparison of molecular tracers within the HC composition in particulate matter and bottom sediments [Nemirovskaya, 2004; Tolosa et al, 2004; Winkels et al, 1998]. Moreover, the HC of aquatic particulate matter is a necessary part of the biogeochemical carbon cycle, because particulate matter represents a transit form of OM on the path from photosynthesis sources to bottom sediments (i.e., the transporting form) [Shiganova et al, 2003].

METHODS

Particulate matter was concentrated on fiberglass filters GF/F. Bottom sediments (oxidized surface and reduced subsurface layers) were collected by an "Ocean" grab.

The procedure of HC extraction and concentration from water, particulate matter, and bottom sediments was strictly standardized. HC were extracted with dichloromethane directly after sampling. Sodium sulfate was added for dehydration during the HC extraction from particulate matter and bottom sediments [Nemirovskaya, 2004].

The extract after dichloromethane removal was dissolved in CCl4, and the bulk extractable fraction (lipids) was determined by IR spectrophotometry at 2930 cm-1 band using a Shimadzu IRAffinity-1 spectrometer. The HC fraction was separated on silica gel using column chromatography. The AHC concentrations were also determined using IR spectrophotometry. A mixture of isooctane, hexadecane, and benzene (37.5, 37.5, and 25 vol. %, respectively) was used as a standard. The alkane concentrations and composition were determined by capillary gas chromatography with an Intersmat GC 121-2 chromatograph (France) using squalane as a standard.

The polycyclic aromatic hydrocarbon (PAH) concentrations and composition were determined by high performance liquid chromatography using a Milikhrom (AcoNova, Novosibirsk, Russia); Nucleosil 100-5C18PAH column; the elutriation media was a mixture of acetonitrile with water (in a 75 : 25 volume proportion). Measurements were performed at 254 nm using a standard of a mixture of individual polyarenes received from a laboratory of the US Environmental Protection Agency. The following unsubstituted polyarenes were identified: naphthalene (NA), phenanthrene (PH), fluoranthene (FL), pyrene (P), chrysene (CHR), perylene (PL), benzo(a)pyrene (BP), anthracene (AN), and triphenylene (TRF) .

RESULTS

The contents of organic compounds in particulate matter varied within the following ranges: 0.18–5.77 mg/l of C_{org}, 130–710 µg/l l of lipids, 90–500 µg/l of AHC and 20–108.6 ng/l of PAH in 2006; and 0.006–0.114 mg/l of C_{org} and 6.2–39.2 µg/l of AHC in 2009. In 2006, the highest concentrations in the coastal waters of the Caspian Sea were found near Tyulenii Island with the maximum at a station where ground dumping takes place because of the navigable canal dredging. In 2003, at a station in the same area [Nemirovskaya and Brekhovskikh, 2008], the AHC content in the bottom sediments was as low as 55.5 µg/g, their fraction within the OM composition was as high as 39.4%, which is usually observed in near-harbor aquatic areas. In the most recent samples of marine bottom sediments from unpolluted areas, the AHC content is only tenths or even hundredth parts of C_{org} [Nemirovskaya, 2004].

Increased AHC concentrations in particulate matter were also registered at a station near the exit from the navigable canal and at a station in the Bakhtemir channel: AHC was 140 µg/l on average with the standard deviation (σ) of 20 µg/l. In the area of riverine and marine water mixing, the content of dissolved and particulate forms of various compounds is controlled by salinity (S) [Lisitsyn, 1995]. At S = 0.2‰, their concentrations grow, which is caused by sorption of emulsified, mainly anthropogenic components, on fine particulate matter (1–10 µm) [Nemirovskaya, 2004]. This is promoted by the presence of large amounts of particulate matter, humic and fulvic acids, iron, and bacteria in the freshwater part of the marginal filter [Lisitsyn, 1995]. At S >0.2‰, due to the loss of aggregative stability of the particles, particulate matter precipitates causing a decrease in the AHC concentrations. Later, at S = 4.6–5.4‰ in the "ooze plug," the AHC concentrations increase again. With the distance from the zones of increased AHC concentrations in the direction of the main water flow, their concentrations varied insignificantly, which may be caused by the small depths and by the supply from the bottom sediments during formation of the nepheloid layer [Kravchishina, 2009; Lisitsyn, 1995]. In the coastal waters of the Caspian Sea, the lipids of particulate matter consist mainly of AHC and a strict correlation between the contents of these compounds was observed: r(lipids–AHC) = 0.93. Their fraction within the lipid composition was 74.7% on average (in oil-polluted areas, the fraction of AHC is usually increased [Nemirovskaya, 2004]). On the contrary, in the composition of C_{org}, lipids were not the prevailing fraction. In most of the samples, their fraction was 25% or below (21.4% on average); the fraction of AHC was 23.4% or below (16.5% on average). The exceptions were found at stations in the Bakhtemir channel, where the fractions of lipids and AHC increased to 65.3 and 48.3%, respectively, which may indirectly point to the presence of oil HC. AHC of particulate matter were characterized by a uniform distribution of alkanes, because the ratio of odd to even homologues (CPI, or the carbon preference index in the high-molecular range) in most of the samples varied within 1.0–1.3, which is characteristic of HC of oil and phytoplankton [Kennicutt and Jeffrey, 1988]. At the stations near Tyulenii Island, the composition of the alkanes is the closest to that of the biogenic substance and shows a bimodal distribution of the homologues (Fig. 2). In the low-molecular range, the maximum is associated with n-C17–C18 (autochthonous alkanes of phytoplankton), while in the high-molecular range the maximum is confined to the n-C25–C27 odd homologues (CPI = = 1.2). High-molecular alkanes prevail: the ratio $\Sigma(C12 + C22)/\Sigma(C23 + C37) = 0.39$. The content of n-alkanes is higher than that of iso-compounds: the ratios i-C19/ n-C17 = 0.53, i-C20/n-C18 = 0.33, and i-C19/i-C20 = 1.7 (prystane/phytane), which is characteristic of autochthonous compounds [Bouloubassi and Saliot, 1993; Kennicutt and Jeffrey, 1988]. The cogged shape of the hump and the presence of the series of iso-compounds are characteristic of biotransformed residues of light oil products [Nemirovskaya, 2004].

In 2006, the content of total PAH (43.7 ng/l on average) was higher than that in open seawaters (20 ng/l) [Nemirovskaya, 2004]. In harbor areas and coastal zones, the concentrations of polyarenes is usually increased. For example, in the Gulf of Riga, the average PAH concentrations in filtered particulate matter were 56 ng/l in the surface and 73 ng/l in the near-bottom waters; the concentration was 70 ng/l in the surface waters of the Sakhalin shelf [Nemirovskaya, 2004]. The variations of the PAH concentrations generally follow the distribution of lipids and AHC, which may point either to the same sources of their formation or to a high degree of transformation of different HC classes.

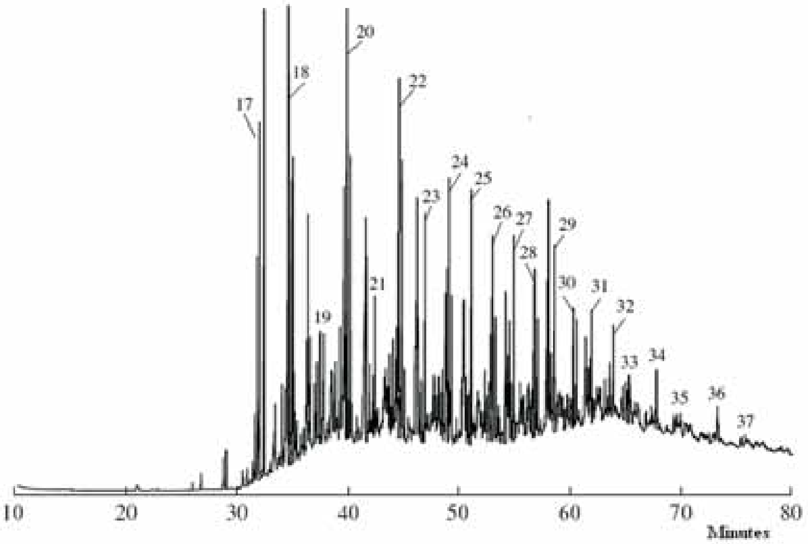

Fig. 2. Chromatogram of the alkanes in an integrated sample of particulate matter from the aquatic area near Tyulenii Island

It is believed that AHC are supplied to the marine environment through their synthesis by phytoplankton, or by oil pollution, and PAH are formed either in pyrolytic processes or under abiogenous natural synthesis [Rovinskii, 1988; Tolosa et al, 2004]. In late summer, with the increase in the air and water temperatures, decomposition of most unstable hydrocarbons takes place [Rovinskii, 1988]. Therefore, the amount and composition of HC depend not only on the sources of their formation but also on their stability in the marine environment. Because of this, the content of prevailing PAH in particulate matter in the area studied decrease in general as the sequence (in %): Ph (34.4) > Fl (20.1) > N (10.8) > BaAn (9.6) > Py (9.4) > An (7.5) >Chr (6.5) > Bp (1.5) > Pl (1.1). We assume that a selective transformation of light polyarenes from dissolved forms into particulate matter by sorption and sedimentation, or by bioaccumulation and biosedimentation takes place [Lipiatou et al, 1993]. The low values of the Fl/(Fl + Py) ratio at stations 9 and 12 (respectively, 0.33 and 0.43) may point to the influence of pyrogenous sources (with the supply of newly-formed combustion products, the value of the Fl/(Fl + Py) ratio is below 0.5) [Tolosa et al, 2004].

The bottom sediments of the coastal waters of the northern part of the Caspian Sea studied in 2005 are mainly presented by sandy sediments containing shells and algae, with a relatively low C_{org} content (0.197–0.582%). The exception is the silty–clayey sediment from station 5, in which C_{org} concentrations increased to 1.199%. The distribution of organic compounds depends, to a great extent, on the degree of sediment dispersion. When passing from sands to silts, the C_{org} value usually increases [Nemirovskaya, 2004]. There was a correlation between sediment dispersion and C_{org} in the area studied: r(C_{org}–moisture) = 0.92 (in 2005), r(C_{org}–moisture) = 0.96 (in 2009). The sediments moisture is determined mainly by their grain-size type. According to our data of 2004, for the surface layer of the sediments from the coastal waters of the Volga River mouth area, r(C_{org}–moisture) = 0.96 [Nemirovskaya and Brekhovskikh, 2008].

The distribution of HC, in most cases, is also determined by the grain-size type of sediments (Fig. 3). Silty sediments (especially when the fraction <0.1 mm prevails) easily absorb organic compounds, including the pollutants from the water mass containing particulate matter. Kaolin and illite have the maximum sorption capability for oil products. Nevertheless, in the area studied, the AHC concentrations in coarse-grained sediments appeared to be higher than those in a fine-grained substance. Their values varied widely both with respect to dry sediment and to the OM composition: 70–4557 μg/g, 3.55–62.5% of C_{org}, in 2005 and 2.0-101.4 μg/g, 03-33.8% of C_{org}, in 2009 (Table 1). In the sediments from the Volga River channels in 2004, in one case, the AHC fraction comprised 24% of C_{org} [Nemirovskaya and Brekhovskikh, 2008]. Only in the sediments of the mouth area of the Severnaya Dvina River, during the spring flood and near oil storages, the fraction of AHC reached 74.5% of C_{org} with the AHC content of 544 μg/g. In marine bottom sediments, the AHC fraction is usually 1% or below, with even lower average values in biological objects. In the planktonic C_{org} and in phytobenthos it is respectively 0.14% and 0.048% decreasing in higher terrestrial plants (tree foliage) to 0.01% [Nemirovskaya, 2004]. The high AHC content in the C_{org} composition of the bottom sediments from the northern shelf of the Caspian Sea and the Volga River may also indicate the impact of oil HC.

In 2005, the maximum of the AHC concentrations was found in the sediments from station 19 (see Fig. 1). In the same area, at the closely located stations 18 and 19, a C_{org} content change by a factor of 1.5 corresponded to a change in the AHC content by a factor of 26.6, which was probably caused by the local supply of oil HC to the bottom sediments. Therefore, only a weak correlation between the distribution of C_{org} and AHC was observed (r = 0.26, n = 16).

The content of alkanes and naphthenic compounds (unresolved complex mixture – UCM) was also maximal at station 19: 194.7

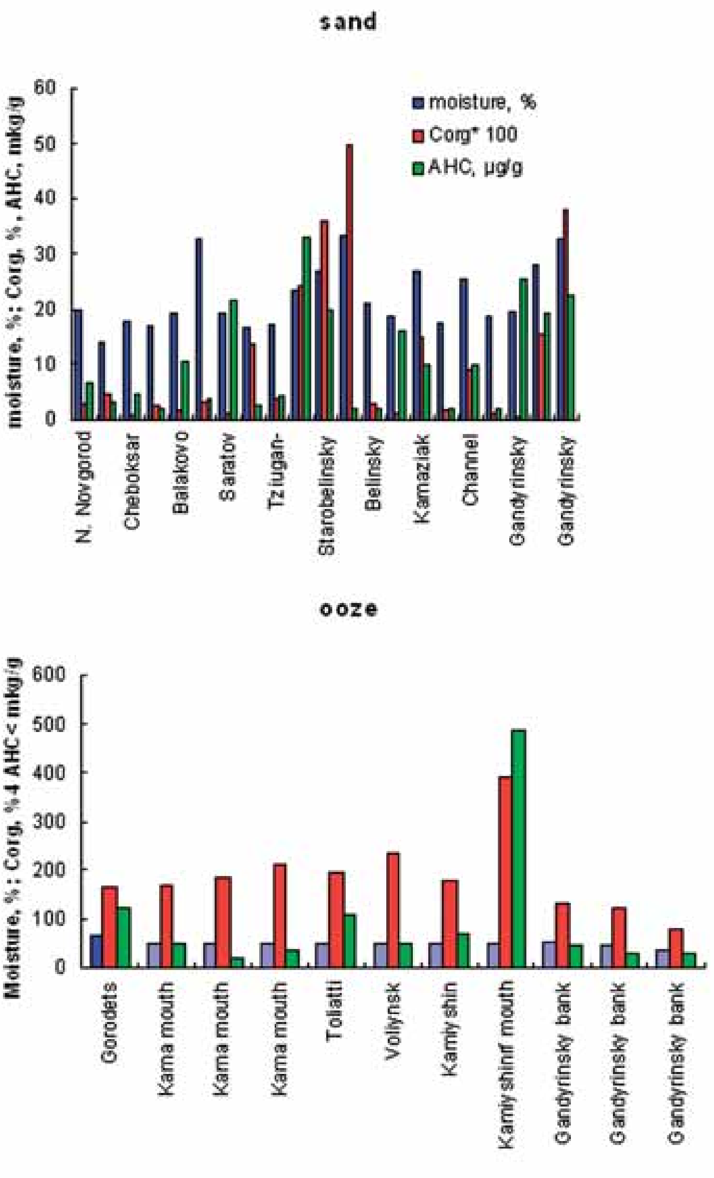

Fig. 3. The distribution of moisture content, C_{org}, and AHC in different grain-size types of sediments in 2009

and 8597 µg/g, respectively, with a maximum naphthene/n-alkane ratio of 44.2, which is characteristic of the HC transformation in the marine environment (for transformed oil alkanes, this ratio is >10 [Tolosa et al, 2004]). Near Baku, at the total n-alkane concentrations in the sediments within 15–17 µg/g, the content of the naphthene–aromatic hump was as high as 1300–1500 µg/g. The values of the ratios of light to heavy homologues in the bottom sediments of this area were quite low (within 0.19–0.69), which also confirms the degree of n-alkane transformation.

According to the distribution of homologues, n-alkanes in the sediments of station 19, as well as in those at stations 17 and 23, were of a mixed origin (Fig. 4). The markers in their composition pointed to the prevalence of biogenic HC: the CPI values varied within

Table 1. Content of C_{org} , AHC and PAH in the surface layer of bottom sediments

Station	Location	Sediment type	C_{org}, %	Moisture,%	AHC,µg/g	AHC, % of C_{org}	PAH, ng/g
1	Gorodez	Gray silt	1.660	65.92	121.4	0.59	32
2	Above N.Novgorod	Sand	0.029	19.95	6.7	1.85	undefined.
3	Oka River mouth	Sand	0.048	14.0	3.0	0.50	“
4	Below Cheboksary	Sand	0.009		4.9	4.36	“
5	Kama River mouth	Gray silt	1.690	50.9	46.8	0.28	33
6	Kama River mouth	Gray silt	1.856	47.7	18.6	0.10	35
7	Confluence of Kama and Volga	Gray silt	2.133	47.29	34.9	0.16	33
8	Tolyatty outer harbour	Gray silt	1.937	46.12	107.4	0.55	145
9	Below Syzran	Sand with shells	2.46	51.18	50.9	0.22	undefined
10	Volynsk outer harbour	Oxidized silt	1.789	49.5	71.3	0.40	“
11	Above Balakovo	Brown fine sand	0.016	19.29	10.6	5.30	16
12	B.Irgiz	Brown fine sand	0.031	32.83	4.02	1.03	26
13	Above Saratov	Brown fine sand	0.012	19.33	21.7	14.47	57
14	Kamishin	Gray silt	1.789	49.5	71.3	0.40	85
15	Confluence of Kamishinka and Volga	Gray silt	3.899	50.24	485.4	1.24	178
16	Below Volgograd	Sand with pebble	0.136	16.55	2.40	0.14	13
17	Zagan-Aman village	Sand with black inclusions	0.036	17.43	4.50	1.00	21
3У	Akhtuba channel	Silty sand with shells	0.245	23.2	33.1	1.08	12
7У	Starobelinsky channel	Silty sand	0.359	27.0	20.2	0.44	2
6У	Joltaya stream (3 km from Starobelinsky channel)	Black ooze	0.499	33.5	2.0	0.03	undefined
9У	Belinsky channel (to the left from waterway)	Dark silty sand	0.029	20.9	2.0	0.55	“
11У	Kamyziak channel (Tabola)	Fine light sand with shell fragments	0.012	18.7	16.1	10.71	“
12У	Kamyziak channel (Verkhnekalinoovsky village)	Sandy silt with clay	0.15	26.8	9.8	0.52	“
14У	Ryty channel	Fine clean sand	0.018	17.8	2.0	0.89	“
15У	3 km above station 14	Dark silty sand	0.091	25.6	9.7	0.85	“
16У	Staraya Volga channel	Fine clean sand	0.011	18.9	2.1	1.45	“
19У	Gandurinsky channel	Clay with fine sand	0.006	19.7	25.3	33.81	“
20У	To the right from station 19 (in macrophyte thicket)	Sand	0.155	28.1	19.0	1.00	29
21У	The same (in open water)	Muddy sand	1.348	54.5	43.0	0.26	24
22У	To the left from station 19 (in a bay)	Muddy sand	1.192	44.1	28.1	0.19	252
23У	The same (in the stream)	Sand	0.38	32.7	23.0	0.47	120
24У	7 km below station 19 (in the channel)	Dark clay	0.807	35.4	29.2	0.29	24

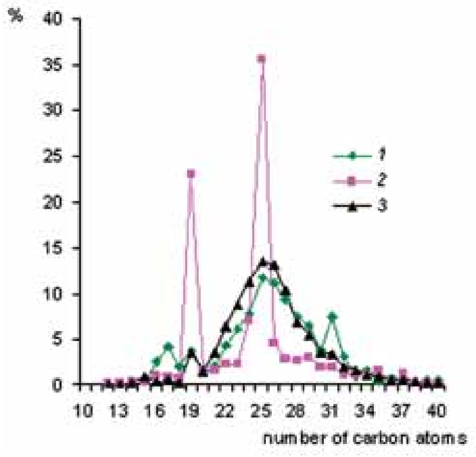

Fig. 4. Composition of the alkanes separated from the bottom sediments in 2005 at stations:

1—18, 2—19, and 3—8
(stations' positions at Fig. 1)

3.05–6.97, and prystane prevailed over phytane (i-C19/i-C20 > 1). Moreover, the maxima at n-C19 and n-C25 may indicate the influence of auto- and allochthonous processes on their composition. In several cases, the maxima were observed in the range of the n-C29–C31 odd alkanes, which is usually related to the contribution of waxes of higher plants [Bouloubassi and Saliot, 1993; Sokolova, Grichyk, 2006]. On shoals, within sandy sediments, oil HC precipitate together with terrigenous substances.

According to the markers, the closest to oil HC were the n-alkanes of the bottom sediments from stations 8, 11, 13, 14, and 18, where CPI ≈ 1 and the naphthene/alkane ratio varied within 10–35.2. Being unresolved by gas chromatography, the UCM is caused by the permanent oil supply in the high-molecular range, and by the transformation natural terrigenous compounds in the low-molecular range [Bouloubassi and Saliot, 1993].

In 2009, in spite of lower concentrations, the composition n-alkane also points to oil origin of AHC (Fig. 5).

In 2005, the dispersion of the PAH concentrations in the bottom sediments was so wide (4–4800 ng/g, see Table. 3) that the average value (948.6 ng/g) was comparable to the standard deviation (σ – 951.2 ng/g). The distribution of PAH, as well as that of AHC, was independent of the grain-size type of sediment, and the maximal values were also found in the sandy sediment of station 19. The content of Bp (the most carcinogenic among the polyarenes identified) at this station was as high as 382 ng/g (12.2% of ΣPAH). The pyrogenous composition of polyarenes in the sediments of this station confirmed the minimal value of Fl/(Fl + Py) ratio, equal to 0.36. At the same time, the (Py + Bp)/(Ph + + Chr) ratio was maximal at station 8, which may point to a high degree of the Tyulenii

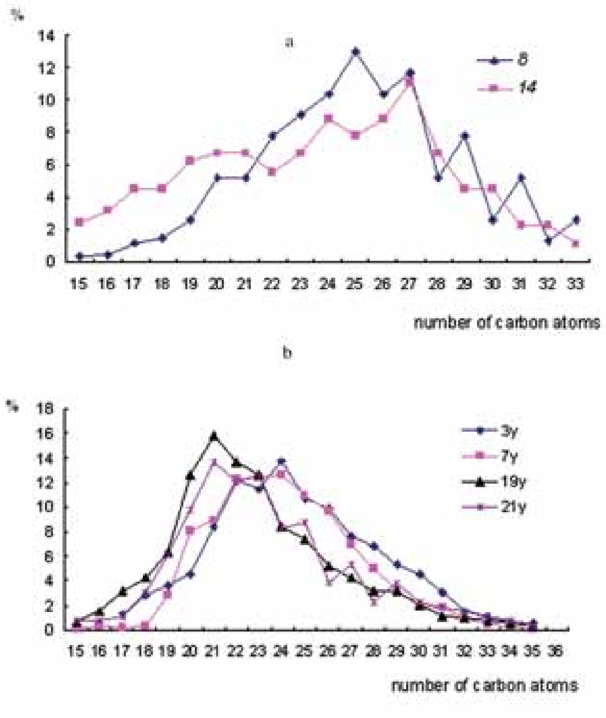

Fig. 5. Composition of the alkanes separated from the bottom sediments in 2009:

station 8 - Tolyatty outer harbor; station 14 – Kamishin; station 3y – Akhtuba channel; station 7y – Starobelinsky channel; station 19y – Gandurinsky channel; and station 21y – Gandurinsky channel (in open water)

Island area pollution with the products of pyrolysis of organic raw materials. The effect of pyrogenous polyarenes was also traced in other areas of the northern part of the Caspian Sea, because (Py + Bp)/(Ph + Chr) ratio in the bottom sediments was over 1 (2.2 on average).

The rather high concentrations of naphthalene characteristic of fresh oil products [AMAP, 2007; Rovinskii et al, 1988] appeared to be unexpected in the sediments of the area studied, because this volatile arene is easily decomposable in the course of natural processes. Its accumulation was noted earlier in the bottom sediments from the shoals of the Apsheron Peninsula and related to oil origin of the polyarenes [Tolosa et al., 2004]. Under the intense transformation in diagenetic processes and with the supply of great amounts of fresh oil compounds, the Ph/An ratio is usually over 10 [Tolosa et al, 2004]. In most of the samples, this value is below 10. Only at station 22, which is the farthest from the main navigable waterways, the Ph/An ratio was as high as 21.7, which may indicate the high degree of transformation of polyarenes in the bottom sediments of this area. According to the markers, the supply of pyrogenous and oil polyarenes to the bottom sediments occurs in the same areas, and a significant correlation between these parameters was observed ($r = 0.61$, $n = 16$). Perylene does not belong to the prevailing polyarenes, despite the fact that significant amounts of it are usually present in the sediments enriched with terrigenous plant matter [Nemirovskaya, 2004; Bouloubassi and Saliot, 1993; Lipiatou et al, 1993; Oros and Ross, 2004]. With the diagenetic origin, the fraction of perylene is over 10% of the total PAH [Tolosa et al, 2004]. In the sediments studied, its content was 6.3% on average. The supply of pyrogenous polyarenes decreases the share of perylene; therefore, the maximal value of the Py/Pl ratio was found in the sediments of station 20 (8.1 at an average of 3.1), which may be related to their supply due to fuel combustion in the navigable areas. At the river–sea boundary (marginal filters [Lisitsyn, 1995]), the principal changes take place in the contents and compositions of the substances supplied by the rivers. Here, in a very narrow zone, the flux of riverine matter decreases by a factor of 10. The AHC sedimentation may reach 80% from their amounts supplied by the rivers [Nemirovskaya, 2004]. In the area of the northern part of the Caspian Sea studied, the effect of the Volga River is expressed in the spread of the flows from the eastern and western channels of the delta, with the latter being more powerful [Shiganova et al, 2003]. This probably resulted in relatively high contents of organic compounds in particulate matter samples collected from the western part of the sea studied. Evidently, intensification of navigation in harbor areas promotes the increase in the HC concentrations in particulate matter.

In riverine waters, particulate OM is usually of a terrigenous nature [Kravchishina, 2009]. In the northern part of the Caspian Sea, the terrigenous OM represented by anthropogenic compounds causes not only an increase in the HC concentrations in particulate matter but also changes in their composition. Oil alkanes become degraded through physical and biochemical processes, especially fast in the surface waters [AMAP, 2007; Nemirovskaya, 2004]. In filtered particulate matter, the autochthonous AHC rarely prevail; mostly, this is a highmolecular anthropogenic group with some components of marine origin [Kennicutt and Jeffrey, 1981], because the content (by mass) of the clayey fraction is negligible [Kravchishina, 2009]. Therefore, in all the samples of particulate matter, high-molecular homologues characteristic of the coastal macrophytes and grassy plants prevail (see Fig. 2). These HC show great capability for hydrophobic binding at the water–particulate matter interface as compared to low-molecular compounds. Only as all the fractions of particulate matter (including fine silt) are precipitated, at the final step of sedimentation, the supply of oil AHC to the bottom may be registered.

In contrast to AHC, in the PAH composition, the light homologues – PH and NA prevail in the composition of PAH of particulate matter. PH is formed in soils from buried biomass [Rovinskii et al, 1988; Venkatesan and Kaplan, 1987] and a high content of it in particulate matter as well as the AHC composition confirm the land origin of aeolic matter. NA and its homologues belong to the arenes prevailing in oil products. The high concentrations of FL may be caused both by anthropogenic impact and by the transformation of the PAH composition during a distant air transfer [Nemirovskaya, 2004], because FL features high stability [Rovinskii et al, 1988]. Hence, the PAH composition in particulate matter is of mixed origin.

The HC content in the bottom sediments appeared to be the highest over the entire time of the studies performed on the northern shelf of the Caspian Sea (see Table 2). Evidently, the area studied in 2005 is associated with the avalanche sedimentation zone, which includes the physicochemical part of the marginal filter [Lisitsyn, 1995]. Here, during the processes of flocculation and coagulation, the bulk of HC is precipitated. Because of this, there is no correlation between the HC distribution and the grain-size composition of the sediments, as well as between HC and C_{org}, which is usually observed in the bottom sediments, even in the areas subject to oil pollution. Thus, a correlation was found between the OM and PAH concentrations in the coastal sediments of Marsalla Lagoon (Italy), although the authors considered the pyrolytical processes to be the main source of PAH [Culotta et al, 2006]. In the mouth of the Severnaya Dvina River, during the spring flood, the composition of n-alkanes conformed to weathered oil HC; at the same time a correlation between C_{org} and AHC was observed (r = 0.72).

In 2005, the content of AHC at stations 10, 17, 19 (1940–4558 µg/g) in coarse-grained sediments was comparable to the concentrations registered in the most polluted harbor aquatic areas [Nemirovskaya, 2004; Nemirovskaya et al, 2007; Tolosa et al, 2004]. The average value of 895.9 µg/g exceeded the background level in silt sediments (50 µg/g). Even at the AHC concentrations of 100 µg/g, the silt sediments are said to be polluted [Tolosa et al, 2004]. In sandy sediments of the Gulf of Riga, the AHC background level was 20 µg/g or below, and only in the sandy– silt matter of harbor aquatic areas did their content increase to 108 µg/g [Nemirovskaya et al, 2007].

In 2005, the composition of AHC in the bottom sediments was of a mixed genesis. Probably, there is a limit to the degree of anthropogenic AHC accumulation. This is true for oil products mainly consisting of HC. Hydrophobic binding of high-molecular alkanes is characteristic, to various degrees, of different fractions of particulate matter, and the bulk of anthropogenic compounds precipitate in the shallow-water zone. In 2009, in spite of lower concentrations, the composition of n-alkane also points to oil origin AHC (Fig. 5).

Moreover, the accumulation of anthropogenic AHC together with terrigenous matter may be explained by poor sorting of the sandy–silt matter in the mouth area of the Volga River. At increased concentrations of anthropogenic AHC in water, even due to passive sorption, their content in sandy sediments may increase [Nemirovskaya, 2004]. Therefore, the degree of anthropogenic pollution of coarse-grained sediments appeared to be higher than that for silt substances. The maximal value of CPI = 6.97, i.e., the maximal value of terrigenous HC, was found in the sediments at station 23 which is the closest to the coast in 2005. Supply of oil HC decreases the CPI value, therefore, the chain length of n-alkanes may be used as a marker of their origin. Thus, in the riverine sediments and in the marine samples near Taiwan Island, the CPI values were 4.08 and 1.70 on average, respectively [Jeng, 2006].

The concentrations of PAH in the bottom sediments sampled in 2005 (on average, 948.6 ng/g), as well as those of AHC, appeared to be the highest during the entire period of the studies since 2003. At stations 10, 11, 17, and 23, the content of PAH was over 1000 ng/g, and over 4000 ng/g, at station 19. Therefore, the fractions of individual polyarenes decreased in the order (in %): Py

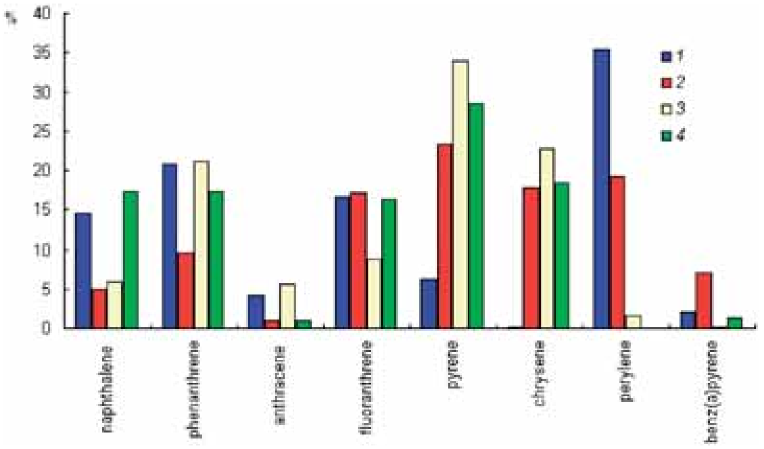

Fig. 6. Composition of PAH separated from the bottom sediments in 2009:

1, 2, 3, 4 — stations: 1 — station 7, confluence of the Kama and the Volga; 2 — station 8, Tolyatty outer harbor; 3 — station 22y, Gandurinsky channel (in the bay); and 4 — station 23y, Gandurinsky channel (in the stream)

(21.1) > Fl (20.1) > NA (19.2) > Pl (6.3) > Bpl (6.0) > Bp (5.6) >An (5.3) > Chr (4.2).

In 2009 in the Volga Delta and the Volga River, the concentrations of PAH in the bottom sediments varied between 2-25 ng/g and 13-178 ng/g, respectively. The markers in the PAH composition of the zone of the avalanche sedimentation mainly pointed to a mixed origin of polyarenes (oil and pyrogenous with a small inclusion of biogenic HC (Fig. 6), that agrees with earlier received results [Sokolova, Ablia, 2007].

The sediments are considered as low-polluted at the content of the sum of 3–6-cyclic polyarenes below 100 ng/g [Tolosa et al, 2004]. In the areas of a permanent supply of pollutants, the concentrations of PAH in the bottom sediments are usually >1000 ng/g; at the values over 4000 ng/g, the sediments become toxic. The content of Bp in the bottom sediments of the area considered exceeded the maximal allowable content for soils (20 ng/g) by factors of 8–19. The concentrations obtained are comparable to those of the most polluted bottom sediments of the Mediterranean Sea. In the area of the northwestern coasts of France, their concentrations varied within 6900–48090 ng/g, and within 72–18381 ng/g, off the Italian coasts [Culotta et al, 2006]. However, despite the high HC concentrations in the area of the avalanche sedimentation, the markers within their composition pointed to their mixed origin (anthropogenic and biogenic).

This may be explained by the fact that, in all natural objects, HC are subject to various physical (weathering and erosion) and chemical (oxidation and photo-oxidation) transformations, as well as to biodegradation by micro-, plant, and animal organisms. Even for the more stable polyarenes, the rate of PAH photochemical transformation is comparable to that of microbiological oxidation of nonaromatic HC of oil. In simulation experiments, it was shown that the destruction of Bp mainly proceeds in the surface layer of the water (53%/h) and, to a considerably lower degree, at a depth of 30 cm (5.6%). The microbial Bp destruction in the surface seawater is about 400 t/year, i.e., about 8% of the total Bp supply from natural and anthropogenic sources [Rovinskii et al, 1988]. Only on the shelf of the Caspian Sea (according to the studies performed in 2004), after passing through the marginal filter, did the AHC concentrations in the bottom sediments decrease, and the alkanes of land vegetation prevailed in their composition. The content of PAH in sandy sediments also decreased here to 3–17 ng/g. The (Py + Bp)/(Ph + Chr)

Table 2. Content of AHC (μg/g of dry weight) in the surface layer of the bottom sediments of the Caspian Sea

Region	Year	AHC	Reference
Azerbaijan shelf	2000	39–1515	Tolosa et al, 2004*
Iranian shelf	2001	14–113	«
Northern part (Russian aquatic area)	2000	1–42*	«
Kazakhstan shelf	2001	2–14*	«
Northern shelf	2003	20–142	Nemirovskaya and Brekhovskikh, 2008
Volga River channels	2004	59–3881	
Northern shelf	2004	94–136	«
Northern shelf	2005	70–4558	«
Volga River	2009	3–121.4	This study
Volga Delta	2009	2–43	«
Antarctica, background	2001, 2003	12–210	Nemirovskaya, 2004

Note: * total alkanes.

ratio decreased from 0.6–11.5 to 0.3–0.5 due to the precipitation of P and BP in the area of the marine and riverine water mixing. Barrier of the Volga River–Caspian shelf acts as a filter preventing the input of anthropogenic HC from the Volga River.

Thus, during the period of the studies from 2003 to 2009, the Volga River and all three areas of the marginal filters of the Volga River – Northern Shelf of the Caspian Sea were examined. The gravitational area, which included the river channels; the physicochemical area, or the zone of the avalanche sedimentation with the highest HC concentrations; and the biological area, where the markers point, to the highest degree, to a natural origin of HC in the bottom sediments. In 2005, the HC content in the bottom sediments appeared to be the highest over all the time of the surveys performed on the northern shelf of the Caspian Sea (Tables 2, 3). Evidently, the area treated in 2005 is associated to the avalanche sedimentation zone, which includes the physicochemical part of the marginal filter [Lisitsyn, 1995]. Here, during the processes of

Table 3. Content of PAH (ng/g of dry weight) in the surface layer of bottom sediments of the Caspian Sea

Region	Year	PAH	Reference
Volga River mouth	1993	40	Winkels, et al, 1998
Azerbaijan shelf	2000	338–2988 (Σ15 PAH)	Tolosa et al, 2004*
Iranian shelf	2001	94–1789 (Σ15 PAH)	
Northern part (Russian aquatic area)	2000	6–345 (Σ15 PAH)	
Kazakhstan shelf	2001	7–294 (Σ15 PAH)	
Northern shelf	2003	3–17 (Σ8 PAH)	Nemirovskaya and Brehovskikh, 2008
Volga River channels	2004	8–154 (Σ8 PAH)	
Northern shelf	2004	6–76 (Σ8 PAH)	
Northern shelf	2005	4–4800(Σ10 PAH)	
River Volga	2009	3–121.4(Σ10 PAH)	This study
Delta Volga	2009	2–43(Σ10 PAH)	

flocculation and coagulation, the bulk of HC is precipitated.

The low concentrations of suspended substances in the surface waters are characteristic of summer steady low water level of the Volga River. Diffusion and dilution play leading role at the confluence of the Volga River and its inflows. The concentration of HC in the surface waters and sediments corresponded to their background levels that indicate insignificant oil pollution. The parameters studied undergo changes under the influence of natural processes. However, increased role of HC in C_{org} in arenaceous sediments of the Volga Delta probably were due to the influence of polluting oil compounds.

CONCLUSIONS

The composition of HC in particulate matter and the bottom sediments in the area of the Volga River estuary undergoes regular changes due to the transformation and precipitation of both anthropogenic and natural compounds. Particulate matter is considerably finer than the bottom sediments, and the grains of biogenic particulate matter do not reach the bottom because of the dissolution in the water mass. Therefore, pronounced distinctions were observed in the composition of filtered particulate matter and the bottom sediments.

The deviations from a simple dilution of riverine OM with marine substances are caused by gravitational, physicochemical, and biological processes. As a result, in the physicochemical part of the marginal filter, in the area of the avalanche sedimentation, the highest degree of the HC accumulation in the bottom sediments takes place (up to 4557.9 µg/g for AHC and up to 4800 ng/g for the total PAH). Because of this, no correlation was observed between the HC content and the grain-size composition of the bottom sediments.

The synthesis of the data obtained in 2003–2009 showed that the geochemical barrier of the Volga River–Caspian shelf acts as a filter preventing the anthropogenic HC from entering the sea.

It is possible that because of this and despite the Volga River supplying a great amount of anthropogenic compounds, the northern shelf is one of the least polluted areas of the Caspian Sea [Tolosa et al, 2004].

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (Presidium of the Russian Academy of Sciences) (Program no. 21 for basic research); project no. 10-05-10084-a. ■

REFERENCES

1. Agatova A. I., K. B. Kirpichev, N. M. Lapina, et al. (2005) Organic Matter in the Caspian Sea / Okeanologiya. Vol. 45. No. 6. pp. 841–850.
2. AMAP (Arctic Monitoring and Assessment Programme) (2007). Chapter 4. Sources, Inputs and Concentrations of Petroleum Hydrocarbons, Polycyclic Aromatic Hydrocarbons, and other Contaminants. Oslo: AMAP. 310 p.
3. Bouloubassi I. and A. Saliot (1993) Investigation of Anthropogenic and Natural Organic Inputs in Estuarine Sediments Using Hydrocarbon Markers (NAN, LAB, PAH) // Oceanol. Acta. Vol. 16. pp. 145–161.
4. Culotta, C. De Stefano, A. Gianguzza, et al. (2006) The PAH Composition of Surface Sediments from Stagnone Coastal Lagoon, Marsalla (Italy) // Mar. Chem. Vol. 99 No 1–7. pp. 117–127.
5. Dumont H. J. (1998) Caspian Lake: History, Biota, Structure, and Function //Limnol. Oceanogr. Vol. 43. pp. 44–52.
6. Efimov I. (2000) The Oil and Gas Resource Base of the Caspian Region // J. of Petroleum Science Eng. Vol. 28. pp. 157–159.
7. Jeng W-L. (2006) Higher Plant n-Alkane Average Chain Length As an Indicator of Petrogenic Hydrocarbons Contamination in Marine Sediments // Mar. Chem. Vol.102. No 3–4. pp. 242–251.

8. Kennicutt M. C. and L. M. Jeffrey (1981) Chemical and GC-MS Characterization of Marine Dissolved Lipids // Mar. Chem. No. 10, pp. 367–387.
9. Kravchishina M. D. (2009) Suspended Particulate Matter in the White Sea and its Grain-Size Distribution. Nauchn. Mir, Moscow. 263 p. [in Russian].
10. Lipiatou, J. Marty, and A. Saliot. (1993) Sediment Trap Fluxes and Transport of Polycyclic Aromatic Hydrocarbons in the Mediterranean Sea //Mar. Chem. Vol. 44. pp. 43–54.
11. Lisitsyn, A.P. (1995) The Marginal filter of the Ocean // Oceanology.Vol. 34, No. 5, pp. 671–682.
12. Methodic Guidelines. (1996) Determination of Pollutants in the Samples of Bottom Sediments. RD 52.10.556-95 Gidrometeoizdat, Moscow. P. 18-26 [in Russian].
13. Methods for Studying Organic Matter in the Ocean (1980) Ed.by E. A. Romankevich Nauka, Moscow. 343 p. [in Russian].
14. Nemirovskaya I. A. (2004) Hydrocarbons in the Ocean (Snow–Ice–Water–Particulate Matter–Bottom Sediments) (Nauchn. Mir, Moscow. 328 p. [in Russian].
15. Nemirovskaya I. A and V. F. Brekhovskikh (2008) Origin of Hydrocarbons in the Particulate Matter and Bottom Sediments of the Northern Shelf of the Caspian Sea // Oceanology, Vol. 48, No. 1, pp. 43–53.
16. Nemirovskaya I A., A.P. Lisitzin and V.P. Shevchenko (2007) Distribution and Composition of Hydrocarbons in Bottom Sediments at the River-Sea Geochemical Barrier // Proceedings of the Tenth International Symposium on River Sedimentation. Moscow. V.4. P.175-184.
17. Oros D. R. and J. M. Ross (2004) Polycyclic Aromatic Hydrocarbons in Estuary sediments // Mar. Chem. Vol. 86. pp.169-184.
18. Rovinskii F. Ya., T. A. Teplitskaya, and T. A. Alekseeva (1988) Background Monitoring of Polycyclic Aromatic Hydrocarbons. Gidrometeoizdat, Leningrad. 224 p. [in Russian].
19. Shiganova T. A., V. V. Sapozhnikov, E. I. Musaeva, et al. (2003) Factors Determining the Conditions of Distribution and Quantitative Characteristics of the Ctenophore Mnemiopsis leidyi in the North Caspian // Okeanologiya. Vol. 43 No 5, pp. 716–733.
20. Sokolova M.N. Grichyk D.V. (2006) Investigation of pollution of bottom sediments of the North Caspian Sea with organic compounds //Vestnik MGU, №6, pp. 16-23. [in Russian].
21. Sokolova M.N. Ablia E.A. (2007) Investigation biomarkers in organic matter of bottom sediments of the North and Middle Caspian Sea // Vestnik MGU, №2, pp. 49-57 [in Russian].
22. Tolosa I., S. Mora M. R. Sheikholeslami M.R. et al. (2004) Aliphatic and Aromatic Hydrocarbons in Coastal Caspian Sea Sediments //Mar. Pollut. Bull. Vol. 48. pp. 44–60.
23. Venkatesan M. J. and I. R. Kaplan (1987) The Lipid Geochemistry of Antarctic Marine Sediments: Bransfield Strait // Mar. Chem. Vol. 21. pp. 347–375.
24. Winkels H. J., S. B. Kroonenberg, M. Y. Lychagin, et al. (1998) Geochronology of Priority Pollutants in Sedimentation Zones of the Volga and Danube Delta in Comparison with the Rhone Delta // Applied Geochem. Vol. 13. pp. 581–591.

Inna A. Nemirovskaya graduated from the Moscow State University Faculty of Chemistry. Now she is the Head of the Analytical Laboratory of the P. P. Shirshov Institute of Oceanology, Russian Academy of Sciences, DSc. in Geology. The focus of research: mechanism of quantitative and qualitative distribution of various classes of natural and anthropogenesis hydrocarbons in all external spheres: atmo-, cryo-, bio-, hydro-, lithosphere in the World Ocean. She took part in many expeditions including those to Arctic and Antarctic regions. Author of 190 scientific works and two books.