Chapter 6. Petroleum hydrocarbons pollution

Subchapter 6.1. Marine waters

Ivanov A., Tkachenko Yu., Derbicheva T., Ilyin Yu., Malchenko Yu., Shibaeva S., Djakov N., Gozhik P., Bagriy I., Ivanova A., Petrenko O., Zhugailo S., Sapozhnikov V., Korshenko A., Panova A., Krutov A., Ermakov V., Kochetkov V., Komorin V., Orlova I., Pavlenko N., Denga Yu., Chasovnikov V., Belyaev N., Kolyuchkina G., Shapovalova E., Simakova U., Nasurov A., Mironov O., Alyomov S., Basar E., Kutaeva N., Pisheva D., Patlatyuk E.

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6.1.13. Summary: Presence of petroleum hydrocarbons in the water

Petroleum hydrocarbons (PHs) belong to the most widespread and hazardous substances to pollute the environment, including marine waters. They negatively affect most of the organisms and the trophic chain in entirety. The PHs presence in the natural water bodies result in the water quality change to become visible because of bacteria increase in number (e. g. PHs oxidizing bacteria); the water organoleptic property change; increase of the dissolved organic substances concentration including such toxic substances as phenols, naphtols, and others; the elevated nutrients concentration; occasionally intensive development of the zooplankton and phytoplankton opportunistic species. Ultimately, PHs are associated with displacement, disturbance or loss of biota — fish and wildlife particularly — as well as loss of habitats, degradation of beaches and many other negative phenomena. The most toxic for marine life PHs are the light fractions.

6.1.1. Major oil spill accidents in the Black Sea region

An oil spill is a release of petroleum into the natural environment. As such, oil flows along the sea surface often reaching the shore and severely damaging rich ecosystems in the shallow waters and life on the coasts. The shoreline habitat may need up to 30 years to recover from a major oil spill. Spill accidents may happen during the oil loading or transportation. Actually, the term ‘oil spill’ often refers to marine oil spills when petroleum is released into the sea from the damaged tankers. Thus, oil tankers are the boats that most likely might cause major environmental damage worldwide including the Black Sea region as well.

During the past 50 years, several accidents of the scale larger than the Kerch Strait disaster have happened in the Black Sea and its straits. Those reported by Turkey are presented in Table 6.1.1a.

Table 6.1.1a. Oil spills from 1960 to 2002 at the Turkish coasts.

Date	Ship Name	Ship Flag	Accident Area	Amount of Oil Spilled	Cause
14.12.1960	*World Harmony, Peter Zoranic*	Greece Yugoslavia	the Bosporus Strait, Kanlica	18,000 tons	Collision and fire
15.09.1964	*Norborn,* Wreck of *Peter Zoranic*	Norway Yugoslavia	the Bosporus Strait, Kanlica	Unknown	fire
01.03.1966	*Lutsk, Krasnyi Oktyabr*	USSR USSR	the Bosporus Strait, Kizkulesi	1850 tons	Collision and fire
10.08.1977	*USSR-1*	USSR	the Bosporus Strait	20 000 tons	Ran a ground
25.12.1978	*Kosmos M*		Akbas, the Dardanelles (Canakkale) Strait	10 000 tons	Unknown
15.11.1979	*Independentia, Evriali*	Romania Greece	Southern entrance of the Bosporus Strait	30 000 tons, got burnt 64 000 tons spilled	Collision and fire
09.11.1980	*Nordic Faith, Stavanda*	Great Britain, Greece	the Bosporus Strait	Unknown	Collision and fire
29.10.1988	*Blue Star, Gaziantep*	Malta, Turkey	the Bosporus Strait, Ahirkapi	1000 tons, ammonium spill	Collision
25.03.1990	*Jambur, Da Tung Shan*	Iraq, China	the Bosporus Strait, Sariyer	2600 tons	Collision
13.03.1994	*Nassia, Shipbroker*	Republic of Cyprus	the Bosporus Strait	9000 tons spilled 20 000 tons burnt	Collision, Got burnt

07.12.1999	*Semele, Shipka*	Belize, Bulgaria	the Bosporus Strait, Yenikapi	10 tons	Collision
06.10.2002	*Gotia*	Malta	the Bosporus Strait, the Emirgan quay	20 tons	Stranding, rammed

The largest in the past 20 years oil spill in the Black Sea occurred when the *Nassia* tanker and the *Shipbroker* cargo vessel collided in the Bosporus Strait on 13 March 1994. *Shipbroker* got totally burnt. The major part of *Nassia*'s cargo (it was carrying 98 600 tons of crude oil) was spilled over into the sea and together with 20 000 tons of burnt oil caused severe marine and air pollution on the Bosporus, and in the Black and Marmara Seas (Cabioc'h F., 1998).

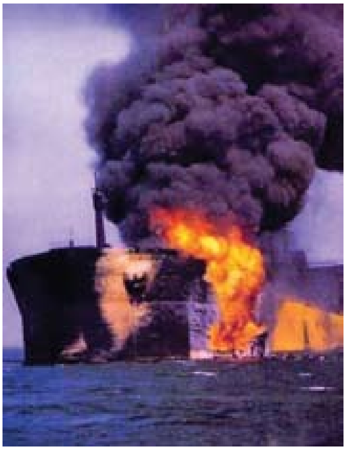

Photo: M/T *Nassia* on 13 March 1994.

In the Marmara Sea, nearly 450 different scale accidents were reported within the last 40 years. One of them was the 1997 accident of the *Trao* tanker that exploded in the Tuzla shipyards located on the North-Eastern cost of the Marmara Sea (Kazezyilmaz M.C. *et al.,* 1998). Some of those events had a severe impact on the environment.

Several ship accidents happened during the past 20 years by the Black Sea coast of Bulgaria, Romania, Russia and Ukraine, however, they mostly brought small-scale oil spills or other kind of pollution.

6.1.2. USSR/UA: Historical data collected in the period of 1981–2007

Between the ports of Crimea and Caucasus located in the narrowest part of the Kerch Strait, routine monitoring of petroleum pollution was started in 1981 (Table 6.1.2a, Fig. 1a). The total number of stations observed in 1981–2007 was 2075, while no observations were carried out in 1987, 1990, 1991, 1993 and 1996. Since 2001, the Opasnoe HMS has monitored regularly TPHs at 100–200 stations on a decadal basis (see Subchapter 5.1 also).

In the late 1990s, petroleum pollution of the Kerch Strait has significantly increased (up to 3 MAC in average, 1 MAC = 0.05 mg/l) in comparison with the early 1990s, and petroleum hydrocarbons were detected in every sample collected. The absolute maximum for the whole period of investigations (2.96 mg/l or 59 MAC) was recorded in October 1982 in the surface waters. Maximal average values in the long-term run were recorded in the period 1995–1998, there is no evidence available whether this elevated level of pollution was related to land-based sources or to shipping. Since

2000, the level of TPHs has decreased to 1–2 MAC with repetition of above 1 MAC concentration in 44–94 % of total samples collected.

Table 6.1.2a. Monitoring stations at the ports of Crimea and Caucasus transect in the Kerch Strait narrowest part.

No	N	E	Depth	Class	Parameters
Opasnoe MHS: the Kerch Strait, the ports of Crimea and Caucasus transect					
6	45°22’24”	36°38’36”	4.7	II	O_2, Alk, S‰, P_{total}, P–PO_4, Si–SiO_4, N–NO_2, N–NO_3, N–NH_4, TPHs, Detergents, Phenols
7	45°22’12”	36°39’00”	7.8	II	The same
8	45°21’54”	36°39’24”	7.5	II	The same
9	45°21’36”	36°39’54”	7.4	II	The same
10	45°21’18”	36°40’12”	7.0		The same
11	45°21’12”	36°40’30”	6.4		The same
12	45°20’56”	36°40’44”	5.8		The same

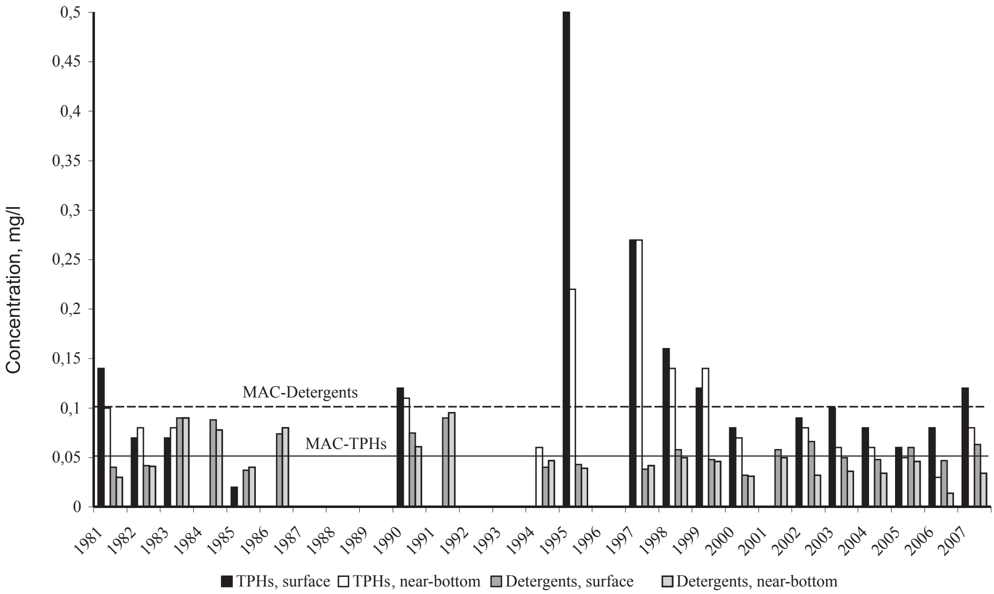

Fig. 6.1.2a. Concentration of petroleum hydrocarbons and detergents in the waters of the Kerch Strait Northern narrowest part in 1981–2007.

In the PHs seasonal dynamics, two periods of low concentrations presence in the Kerch Strait waters (below 1 MAC) are distinguished traditionally, i. e., in winter (January-February), and in summer (July-August), (Fig. 6.1.2b). Correspondingly, maximal levels are recorded in autumn (September-November) and spring (April-June). The minima and maxima can be interpreted as follows. In winter the wind-wave activity grows, while in summer the water temperature raises, and the former and the latter facilitate the decrease in concentrations of TPHs. In spring (before the high water of the rivers Don and Kuban), and in autumn the frequency of the Black Sea flow (from the Black to the Azov Sea) is increased, and this flow brings polluted waters from the transshipment areas to the narrowest part of the Kerch Strait, where the Ukrainian monitoring takes place.

In the Kerch Bight waters n 1992–2000, an average content of TPHs sustained 0.01–0.13 mg/l (Zhugailo S. S. *et al.,* 2008). The maximum concentrations were re-

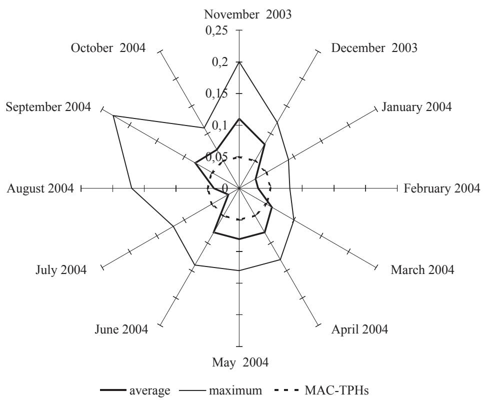

Fig. 6.1.2b. Seasonal distribution of petroleum hydrocarbons concentration in the waters of the Kerch Strait Northern narrowest part in November 2003 — October 2004.

corded in the shipyard vicinity where too many boats were usually brought for temporary anchoring. Also, the local Primorskaya river could have been an additional source. The bight coastal zone was heavily polluted and PHs were the main impacting pollutant throughout the 1990s (Petrenko O.A., 2008). Later on, in 2000–2007 the TPHs presence level increased further on to reach 0.04–0.28 mg/l (Fig. 6.1.2c).

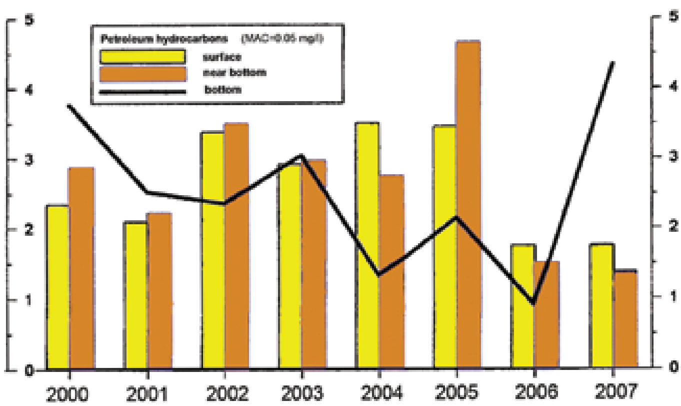

Fig. 6.1.2c. Annual average concentration (mg/l) of total petroleum hydrocarbons in the Kerch Bight waters in 2000–2007 (Zhugailo S. S. *et al.,* 2008).

YugNIRO, Kerch conducted numerous oceanological field investigations in the Kerch Strait area. The institute is located at the strait Ukrainian coast and is engaged with monitoring the Kerch Strait environmental conditions. From 2002 and till the Kerch Strait catastrophe, YugNIRO carried out eight expeditions in the Strait, measured petroleum hydrocarbons levels and — in addition — surveyed the standard hydrochemistry parameters (incl. nutrients), trace metals and chlorine hydrocarbons as well as the plankton and benthos communities. In 2002–2007, altogether 184 stations were sampled and in total 191 water samples and 147 bottom sediment samples were collected. The expeditions description is given in Annex 2.

6.1.3. Observations after the Kerch Strait accident

Numerous scientific investigations were conducted after the Kerch Strait accident of November 2007 and an obvious overlapping of different institutions activities happened in their course. Some of the studies conducted included visual observation of the Kerch Strait sea surface and shoreline. The main purpose of investigations was to find out, where and in what area the heavy fuel oil released from the *Volgoneft-139* tanker had spread over and — finally — where it had arrived at the coast to. Simultaneously, information/data required for damage assessments of the accident were collected. Few expeditions engaged the divers to do the underwater direct observations of the marine ecosystem status to include large animals like mussels and marine grasses. Most numerous were traditional oceanographic expeditions to collect the samples onboard, i. e., hydrological and hydrochemical, though not only. A special attention was paid to marine waters, bottom sediments and biota extent of pollution by sulphur, pesticides, PCBs, PAHs and trace metals. In total, about 60 different complex cruises were conducted in 2007–2009 (after the Kerch Strait accident) by various Russian and Ukrainian scientific institutions. The list of expeditions is presented in Annex 2.

The following Russian institutions were engaged with extensive studies of the Kerch Strait accident consequences: the Shirshov Institute of Oceanology (Moscow) and its Southern Branch (Gelendzhik), the RAS Southern Scientific Center (Rostov-on-Don), AzNIIRKH (Rostov-on-Don), the Kuban Estuarine Station (Temruk) and the Black-Azov Seas Directorate (Novorossiysk). In Ukraine, complex investigations were carried out by the Marine Hydrophysical Institute (MHI), Institute Biology of the Southern Seas (IBSS) and the UHMI Marine Branch (all from Sevastopol), YugNIRO (Kerch) and UkrSCES (Odessa). Many scientists and technical experts took part in the samples analysis, and database and materials compilation. The lists of leading scientists and institutions who participated in different investigations are presented in Annexes 1 and 4 correspondingly.

6.1.4. UA: National Monitoring System. The Kerch Strait in 2007–2009

At the ports of Crimea and Caucasus transect located in the Kerch Strait Northern narrowest part, 35 cruises were carried out by the Opasnoe HMS of the Ukrainian Hydrometeorological Service in April-November 2008 and April–June 2009. Four permanent stations have been regularly observed in the frameworks of the Ukrainian routine monitoring program (Fig. 1a, see Chapter 1), Table 6.1.2a, stations No 6–9).

In 2008, 280 samples were collected and numerous hydrochemical parameters were studied in parallel with petroleum hydrocarbons (Chapter 5). TPHs concentrations varied from analytical zero to 0.31 mg/l (6.2 MAC) in the bottom layers, while reaching up to 0.24 mg/l at the surface. The maximum was observed in August in the near-bottom layer close to the port of Caucasus. The TPHs average value for the water column was 0.06 mg/l, i. e., 1.7 times lower than in 2007, though in general it remained at the typical for the area annu-

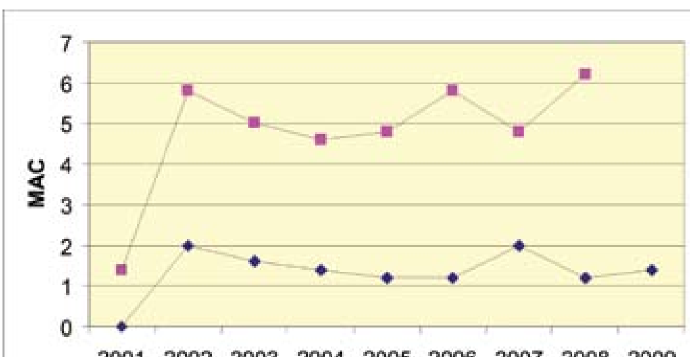

Fig. 6.1.4a. TPHs concentration, average (blue) and maximum (rose), expressed in MAC in 2001–2009.

al level (Fig. 6.1.4a, Table 6.1.4a). Majority of samples collected in 2008 contained TPHs exceeding the level of 1 MAC. In 2009, their average level slightly exceeded 1 MAC.

Table 6.1.4a. TPHs concentration (annual average — above and maximum — below in mg/l (C*) and expressed in MAC) detected in the Northern narrowest part of the Kerch Strait at the transect of the ports of Crimea and Caucasus.

2001		2002		2003		2004		2005		2006		2007		2008		2009	
C*	MAC	C*	MAC	C*	MAC	C*	MAC	C*	MAC	C*	MAC	C*	MAC	C*	MAC	C*	MAC
0	0	0.10	2.0	0.08	1.6	0.07	1.4	0.06	1.2	0.06	1.2	0.10	2.0	0.06	1.2	0.07	1.4
0.07	1.4	0.29	5.8	0.25	5.0	0.23	4.6	0.24	4.8	0.29	5.8	0.24	4.8	0.31	6.2	–	

6.1.5. UA: YugNIRO. November 2007 and February, April, May 2008

Investigation on TPHs content in the UA coastal waters was conducted shortly after the Kerch oil spill, on 15th November 2007 at the site of the Kerch municipal pear. TPHs concentration was registered as 1.0 and 1.3 MAC to decrease later below 0.05 mg/l. Shortly later on 22 November it was registered again increased to 2 MAC, however, the next day again TPHs fell down to 1.5 MAC and thus continued fluctuating further on at the levels typical for the Kerch Strait coastal waters. Also, heavy fractions of oil hydrocarbons had their maximum of 0.037 mg/l on 22 November in contrast to their typical concentration of about 0.010 mg/l.

Observations close to the Tuzla Island were conducted on 21 November 2007, and they revealed a low level of hydrocarbons in the upper layer (0.024–0.025 mg/l), as well as in the near-bottom layer (0.026–0.044 mg/l). All the data showed the levels below 1 MAC to equal 0.05 mg/l (Petrenko O.A. *et al.,* 2008). After the oil spill accident in the Kerch Strait on 11 November 2007, petroleum pollution was registered exceeding the level revealed by the August 2007 data collected in the surface and near-bottom layers, i. e., 0.03–0.14 and 0.04–0.09 correspondingly (Zhugailo S.S. *et al.,* 2008).

Three months later on 7 February 2008, TPHs concentration was down by 1.3 times in average. Heavy oil fractions in concentrations were decreasing faster, by 4.2 times in average.

By the end of April 2008, the level of petroleum had increased possibly in the result of secondary pollution. The maximum levels were to the north of the Tuzla Island: in surface waters — 0.128 mg/l or 2.6 MAC and in the near-bottom waters — 0.219 mg/l or 4.4 MAC. In comparison with the previous expedition results, the light (less-transformed) fractions concentration was registered increased by 7 times in average. One of the reasons could be the light fraction washing out from the bottom sediments. For instance, in the vicinity of *Volgoneft-139* the light fractions concentration was found increased by 1.5–2.0 times in the water column, whereas it was registered reduced by two times in the bottom sediments at the sunken tanker bow site, and by almost 8 times — close to the grounded stern.

In May 2008, the TPHs maximum concentration (0.09 mg/l or 1.8 MAC) in the surface waters was registered in the central part of the Strait, while the concentrations were recorded decreased to 0.034 mg/l to the South.

6.1.6. UA: IBSS. 9–17 December 2007

Total petroleum hydrocarbons concentrations in the coastal waters of the Tuzla Island and some other sections of the Kerch Strait were investigated by IBSS within the short period of 9–17 December 2007 (Tab. 6.1.6a). In the vicinity of the Tuzla Island, TPHs level exceeded

1 MAC in 58 % of samples collected. In the period of 14–16 December, practically all sites around the Tuzla Island showed the concentration of 1.5–4 MAC. It was probably related to heavy fuel oil arrival to the Tuzla Island coast following the Kerch Strait accident. Still after its organized collection, some oil continued remaining on the sandy beaches, while its small amounts were washed back into the sea. In all the other parts of the Kerch Strait, TPHs concentration exceeding MAC was recorded in 18 % of the samples. In the Azov Sea areas nearest to the Kerch Strait, i. e., the so called Reefs Bight, the hydrocarbons content in water did not exceed the MAC value (checked on 12 December 2007).

Visual observations of December 2007 have clearly showed decrease of water pollution levels compared to the situation right after the Kerch Strait accident. However, when the concentration is below 0.15 mg/l, oil is not visible on the surface and could be detected by chemical analysis only, since it is present in the form of a fine-dispersed emulsion. The process of oil transformation speeds up with increase in wind velocity. Oil film on the surface was registered before in the course of experiments to last 1.5–2 hours with a wind of about 10–15 m/s (Mironov O. G., 1985). High speed of oil transformation from a surface film into a water column emulsion was proved by mathematical modeling as well (Ahmetov A. Sh., 1977, Beliaev V. I., 1974). In the case of the Kerch Strait accident, visible oil slicks disappeared fast from the surface because of a stormy weather. Chemical analyses have proved the presence of elevated TPHs concentrations in December 2007. Nevertheless, TPHs concentrations close to those levels were registered over the whole Azov Sea area in November 1992, while in certain sea areas TPHs were detected at the level of 20 MAC, though no accident had been reported (Mironov O. G., 2000).

Table 6.1.6a. Total petroleum hydrocarbons concentration (mg/l) in the coastal waters of the Kerch Strait on 9–17 December, 2007 (Eremeev V. N. *et al.*, 2008).

Site	09	10	11	12	13	14	15	16	17
The Tuzla Island, North-Western side of the pier	0.05			0.07	0.05	0.11	0.05	0.08	
The Tuzla Island, Western side of the pier	0.17	0.05			0.05	0.14	0.11	0.08	
The Tuzla Island, North-Western extremity	0.05			0.05	0.05	0.11	0.08	0.07	
The Tuzla Island, South-Eastern extremity				0.05					
The Tuzla Island, Southern part	0.05	0.05		0.17	0.19	0.12	0.08	0.08	
The Gleiky Village, coast line in the Light Cape vicinity		0.07	0.05	0.05	0.05	0.05			0.05
The Zukovka village, Putina Ltd.				0.05	0.05	0.05			0.05
The Kiev holiday hotel					0.05	0.08			
The Arshintsevkaya Spit, the Kerch municipal beach					0.05	0.05			
The Azov Sea, the Reefs Bight				0.05					
The Light Cape, a beach toward the Osovino village					0.05				
The Bulganak Bight, WWTP outlet				0.05	0.05	< 0.05			0.05
A dam between the Tabichskoe lake and the Kerch Strait						0.07			
The Varzovskaya Bight		0.08	0.05						

6.1.7. UA: MHI and MB UHMI. Observations in the Kerch Strait in December 2007, March 2008 and December 2009

The Marine Hydrophysical Institute (Sevastopol) conducted in the Kerch Strait region two expeditions to study the level of water and bottom sediments petroleum hydrocarbons pollution in December 2007 and March 2008 (Fig. 6.1.7a)

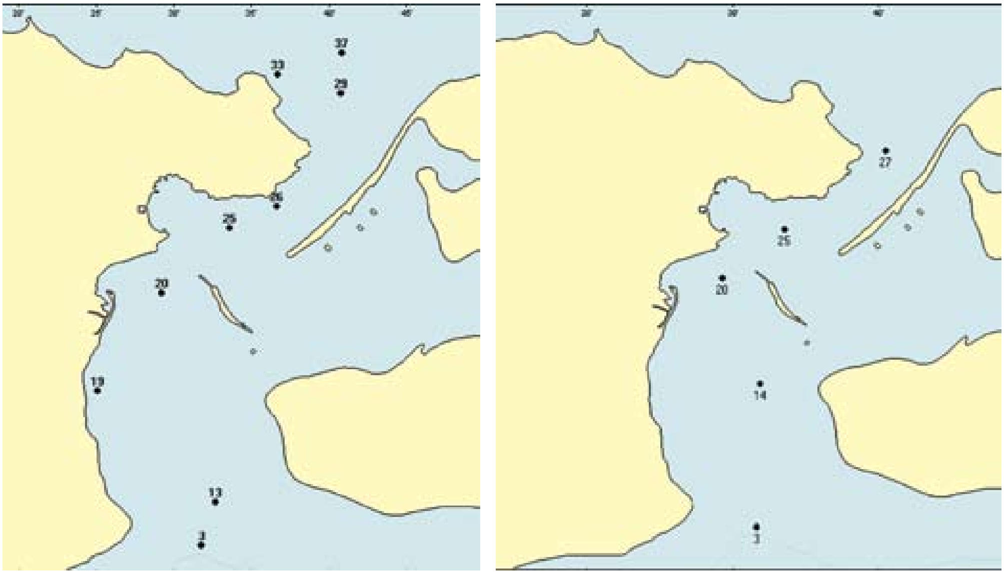

Fig. 6.1.7a. Stations for sampling water and bottom sediments in the Kerch Strait on 6–9 December 2007 and March 2008.

The TPHs upper layer concentration varied in the range below detection limit of 0.02 mg/l to 0.09 mg/l. Above 1 MAC (0.05 mg/l) concentration was recorded at No3 station located in the Black Sea close to the Southern entrance of the Kerch Strait and the site of dredged spoils dumping. Also, close to it was located the area where transshipments from one boat to another were taking place in the Kerch Strait.

On 4 December 2009, the surface water sampling for PHs was carried out by MHI and MB UHMI at 18 stations close to the Tuzla Island (Fig. 6.1.7b). TPHs concentrations were below their detection limit of 0.05 mg/l at all surveyed locations.

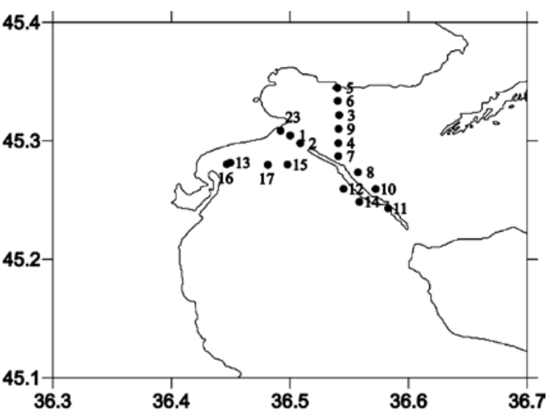

Fig. 6.1.7b. Stations for total petroleum hydrocarbons sampling of the Kerch Strait surface layer on 4 December 2009 (by MHI and MB UHMI).

6.1.8. UA: UkrSCES. The Kerch Strait in July and December 2009 (30th and 31st cruise of the Vladymyr Parshin *RV)*

During the *V. Parshin* RV 30th cruise, investigations of total petroleum hydrocarbons by means of infra-red spectrophotometry (Oradovsky S. G., 1993) and aromatic hydrocarbons — by spectrofluorometry (*Methodic Guidelines*, 1993) were carried out at 14 stations on 8 July 2009 (Fig. 5.6a). Prior to that, samples were collected as well at eight shelf stations in the North-Western part of the Black Sea. Sampling was carried out of the surface layer only. TPHs concentration stood at 1 MAC (Tab. 6.1.8a) at all the Kerch Strait stations with the exception of one. On the contrary, at the Karkinitsky Bay North-Western shelf, TPHs content was reaching 10 MAC. The minimum level was recorded by the Crimean coast. Polyaromatic hydrocarbons were present in low concentration along the Crimean coast as well.

Table 6.1.8a. Total petroleum hydrocarbons and aromatic hydrocarbons concentrations detected in July 2009 in the surface waters of the Black Sea North-Western part and in the Kerch Strait.

Stations	Date	Depth, m	Sampling, depth	Coordinates		TPHs	Aromatic hydrocarbons
				Latitude	Longitude	mg/l	µg/l
the Black Sea North-Western shelf							
4	1.07	26	0	45`47°90	31`22°63	0.05	12.9
5	1.07	38	0	45`39°56	31`36°68	0.57	
6	2.07	44	0	45`31°00	31`41°02	0.26	10.8
7	2.07	50	0	45`14°99	31`37°62	0.08	15.8
98	2.07	45	0	45`24°97	31`21°90	0.13	27.3
99	2.07	45	0	45`25°04	31`13°00	0.09	12.3
100	2.07	51	0	45`15°00	31`20°02	0.05	12.1
96	2.07	58	0	44`56°96	31`29°47	0.02	15.2
the Kerch Strait							
55к	8.07	4.6	0	45`17°95	36`29°26	0.05	33.1
54к	8.07	5	0	45`17°77	36`29°28		12.8
49к	8.07	5	0	45`14°95	36`29°26	0.05	24.2
47к	8.07	6	0	45`14°12	36`30°75		10.6
40к	8.07	7	0	45`11°08	36`25°42	<0.02	28.8
41к	8.07	6	0	45`11°21	36`26°57	0.05	29.2
39к	8.07	18	0	45`09°21	36`27°05	0.05	
44к	8.07	9	0	45`11°82	36`30°63	0.05	21.2

In December 2009, during the 31st *Vladymyr Parshin* RV cruise samples were collected in the Kerch Strait surface and near-bottom waters. In both layers and almost at all stations TPHs concentration exceeded the level of 1 MAC (Fig. 6.1.8a). In the surface waters, a visible patch of high TPHs concentration was registered at the Black Sea entrance to the Kerch Strait (transshipment and anchoring area, where crude oil or oil products were pumped from one ship to another). Higher TPHs levels were also detected in the area westward of the Tuzla Island and in the Strait Northern part by the Chushka Spit. In general, petroleum hydrocarbons content was substantially higher in the near-bottom waters. In the Kerch Strait Northern and Western sections the TPHs distribution patterns were nearly identical in the surface and bottom waters. Quite the opposite, no patch of high TPHs levels near bottom resulting from the higher concentration on the surface was found in its Southern part.

In addition to the infra-red methods applied for TPHs registration, spectrofluorimetric methods for polycyclic aromatic hydrocarbons detection (PAHs) were employed for analysis of the same water samples. Aromatic oil fractions were widely distributed in the Kerch Strait waters and their concentration was reaching the level of 7 μg/l. Their spatial distribution was quite similar to the TPHs presence in the surface layer (Fig. 6.1.8b).

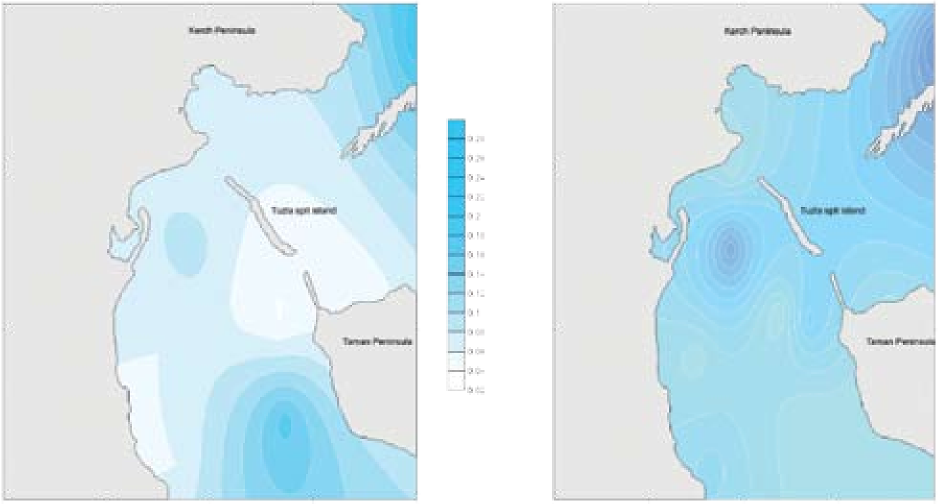

Fig. 6.1.8a. Spatial distribution of total petroleum hydrocarbons (mg/l) in the surface (a) and near-bottom layers in December 2009, the *Vladymyr Parshin* RV 31st cruise.

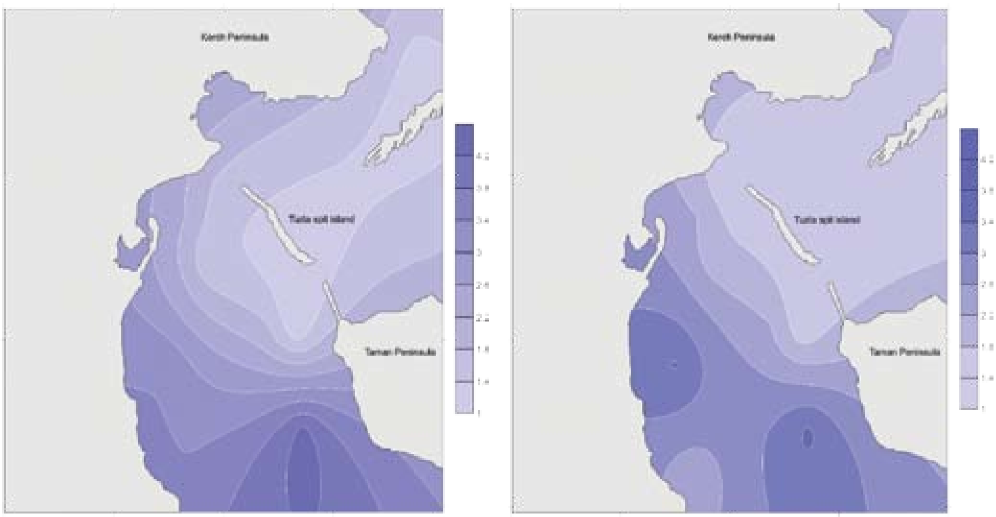

Fig. 6.1.8b. Spatial distribution of aromatic hydrocarbons (μg/l) in the surface (a) and near-bottom layers in December 2009, the *Vladymyr Parshin* RV 31st cruise.

6.1.9. Petroleum hydrocarbons inter-seas exchanges in 2008–2009

The available monitoring data have allowed to determine TPHs exchanges between the Azov and Black Seas through analyzing measured concentrations and calculated water flows (Chapter 5).

Calculations of the water flows and TPHs concentration have revealed high presence of petroleum hydrocarbons in the Azov Sea resulting from the inflow of about 20–660 g/s of TPHs in April-September 2008. However, the opposite flow was registered from October 2008 till May 2009 to result in about 85–300 g/s of TPHs arriving to the Black Sea (Fig. 6.1.9a).

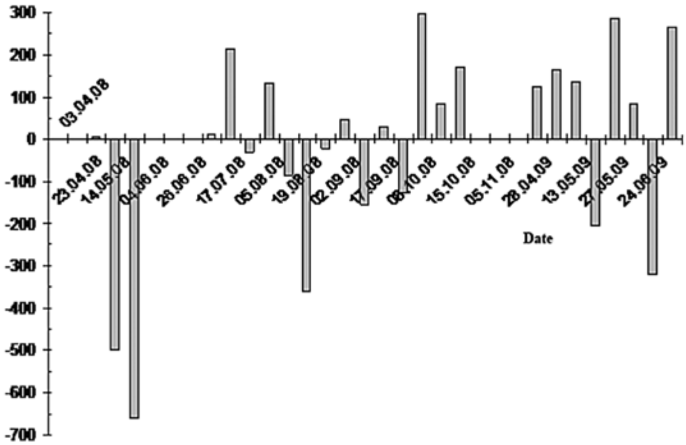

Fig. 6.1.9a. Petroleum hydrocarbons exchanges (g/s) between the Azov and Black Seas in 2008–2009. Minus means flow from the Black to Azov Sea, plus — backward.

6.1.10. RU: Kuban HMS. Monitoring of the Russian waters in 2007–2009

The sea water samples were collected in the surface and near-bottom coastal waters of the Kerch Strait Russian section by the Estuarine Hydrometeorological Station «Kuban» (EHMSK, the town of Temruk) of the Krasnodar Center of Hydrometeorological

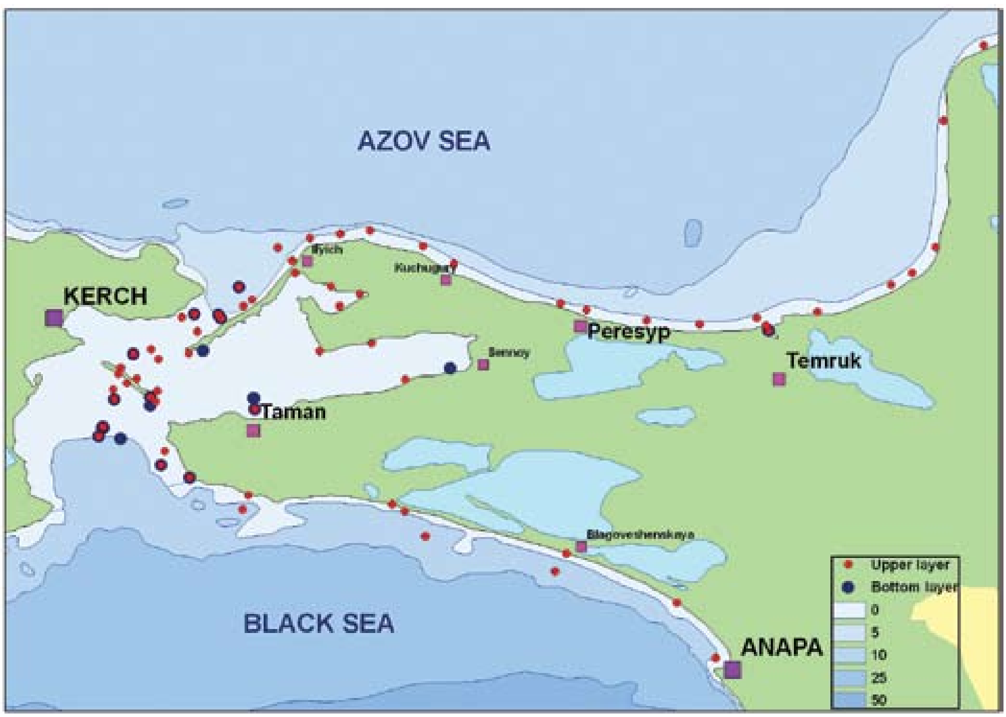

Fig. 6.1.10a. Location of sampling stations: The Russian Roshydromet monitoring program, 13 November 2007 — 29 June 2009.

Service state department under Roshydromet. Petroleum hydrocarbons concentration was determined by means of infrared spectrophotometry (Oradovsky S. G., 1993). During the period of 13 November 2007 — 29 June 2009, 617 samples were collected at 77 stations in the surface waters and 46 samples at 22 stations — in the near-bottom waters (Fig. 6.1.10a). A number of samples were also collected along the Russian coast near Arkhipo-Osipovka, Divnomorskoe, Kabardinka and Abrau-Durso settlements at the stations located far to the South from the Kerch Strait.

During the period of observation, the surface layer regular sampling (two times per month) was carried out at 14 stations out of total 77 only (Fig. 6.1.10b). Generally, monitoring was conducted most regularly at the littoral stations of the Temruk Bay. Still, periodical sampling at the littoral stations located in the Northern and Southern parts of the Tuzla Island and in the Southern part of the Taman Peninsula was carried out as well. Regular sampling and measurement of petroleum hydrocarbons presence in the bottom layers of the Temruk harbor were performed twice at the shipwreck site in the Kerch Strait and close to the Taman village on 28 November and 12 December 2007 respectively.

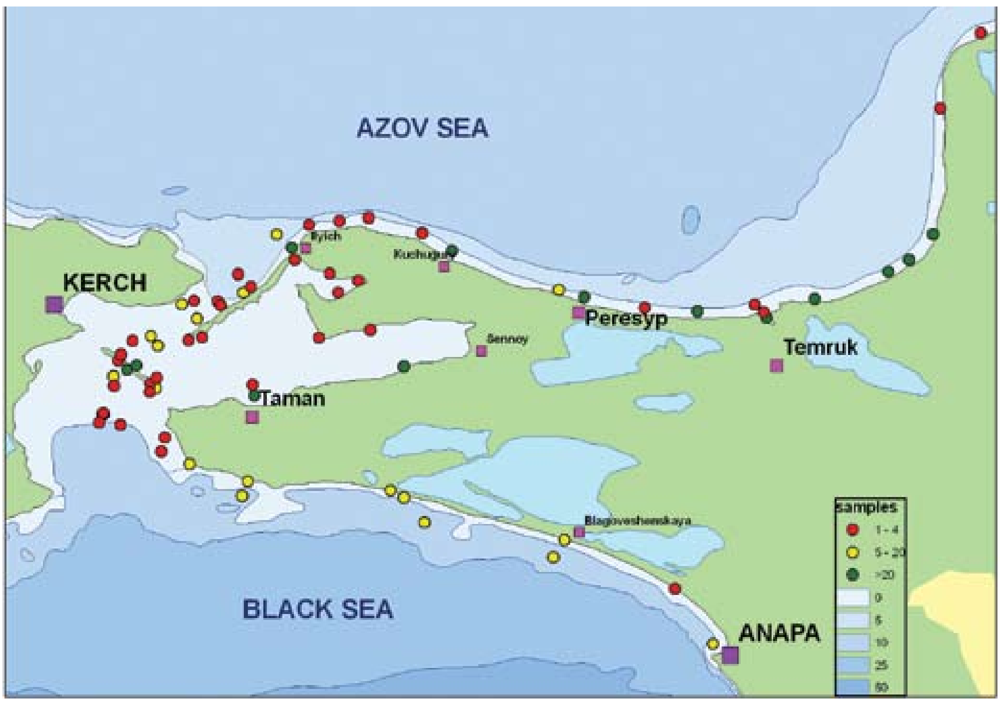

Fig. 6.1.10b. Frequency of the surface layer water sampling on 13 November 2007 — 29 June 2009.

Time dynamics of petroleum pollution: During the observation period of one and a half years (November 2007-June 2009), the highest petroleum hydrocarbons presence level was observed during the first several days after the Kerch Strait accident. It averaged 1.1 mg/l (23 MAC) on 13–16 November 2007. The maximum concentrations of 2.5 mg/l (50 MAC) and 1.74 mg/l (34.7 MAC) were recorded at the shorelines of the Chushka Spit (4 km to the North-East from the port of Caucasus) and of the port of Caucasus respectively.

In the second half of November 2007 sampling was carried out daily. In 24 samples collected on 17–28 November 2007, the TPHs concentration level stood at 0–0.290 mg/l

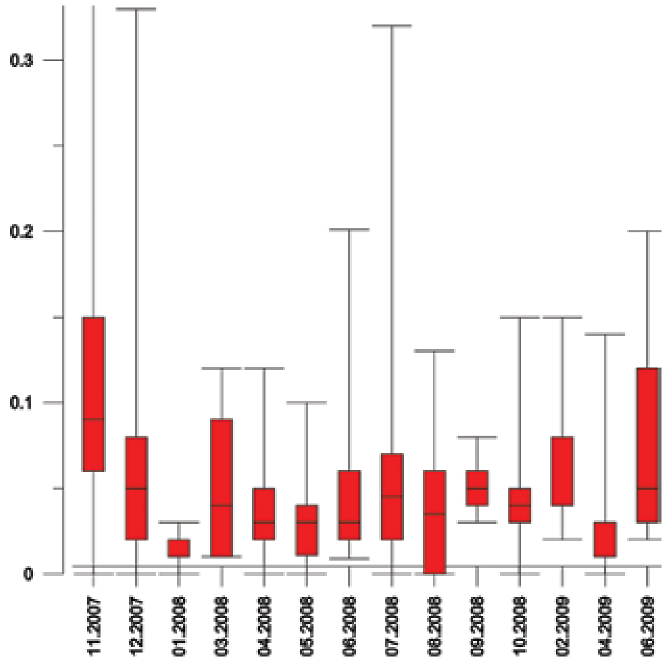

Fig. 6.1.10c. Average monthly presence of petroleum hydrocarbons (mg/l) in the Kerch Strait waters as observed on 13 November 2007 — 3 June 2009. Two maximal values 2.500 mg/l and 1.736 mg/l in November 2007 are not presented at the figure. The box-whisker plot graph displays the minimum, maximum, median, lower quartile, and upper quartile for TPHs.

averaging 0.092 (1.8 MAC). Its highest was recorded in the waters close to the Tuzla Spit. In December 2007, 100 samples were collected in the course of three campaigns and the maximum registered level was 0.330 mg/l (6.6 MAC) recorded on 1 December nearby the Ilyich village. The minimum of 0.001mg/l (0.02 MAC) was observed nearby the port of Temruk and close to the Tuzla Island (from the Taman Bay side) and its average in December was 0.060 mg/l (1.2 MAC). Results obtained in 2007–2009 are presented in Table 6.1.10a.

Table 6.1.10a. TPHs (mg/l) presence in the surface layers: Ranges of variation, averages and areas of maximal concentration, 2007–2009.

Month	**2007**		**2008**									**2009**		
	11	**12**	**01**	**03**	**04**	**05**	**06**	**07**	**08**	**09**	**10**	**02**	**04**	**06**
Range	0–2.500	0–0.330	0–0.030	0.010–0.120	0–0.120	0–0.100	0.009–0.201	0–0.320	0–0.130	0.030–0.080	0–0.150	0.020–0.150	0–0.140	0.020–0.200
Average	0.150	0.060	0.014	0.051	0.034	0.032	0.042	0.051	0.036	0.050	0.044	0.061	0.023	0.074
Average in MAC	3.0	1.2	0.3	1.0	0.7	0.6	0.8	1.0	0.7	1.0	0.9	1.2	0.5	1.5
Max values at:	the Chushka Spit, the Port of Caucasus	the Ilyich village	the Port of Temruk, the Tuzla Spit, the Taman Bay	the Port of Caucasus, the Ilyich village	the Taman village	the Ilyich village	the Tuzla Spit	the Beregovoy village (the Dinsky Bay)	Shipwreck near the Tuzla Island	the Perekopka village in the Temruk Bay	the Perekopka village, the Tuzla Spit	the Panagia Cape	the Temruk port	the Ilyich village

Spatial variability: average TPHs concentration at different sites. Monthly average of TPHs concentration varied significantly at different sites along the coasts of the Kerch Strait and in the Azov Sea (Table 6.1.10b). The most frequent excess of TPHs (ranging 1.5–3 MAC) was observed in 2008–2009 close to the Taman village and the Tuzla Island from the Black Sea side, as well as nearby the Ilyich village and the Port of Caucasus. Concentrations of TPHs lower than 1 MAC were recorded in 220 samples (one third of all samples).

In the near-bottom layer, TPHs concentrations varied from 0.01 mg/l (0.2 MAC) to 0.18 mg/l (3.6 MAC) averaging 0.07 mg/l (1.5 MAC). On 28 November 2007, the maximum of 0.18 mg/l was observed by the Taman village and 2 km to the North, and the minimum concentration of 0.06 mg/l was registered at the head of the sunken tanker. Later, on 18 December 2007 the maximum TPHs concentration of 0.06 mg/l (1.2 MAC) was observed in front of the Panagia Cape close to the Tamansky transshipment site, while the minimum of 0.02 mg/l (0.4 MAC) was recorded by the Port of Caucasus.

Table 6.1.10b. Average TPHs (in MAC) presence in November 2007 — June 2009 as observed in the Kerch Strait surface layer at 16 stations.

Site and number of samples	2007		2008									2009		
Month	11	12	01	03	04	05	06	07	08	09	10	02	04	06
Ilyich village/30	5.2	2.7	0.3	2.4	1.0	1.6	1.1	1.6	0.8	1.3	0.8	1.2	1.2	4.0
Cuchugury village/30	3.6	2.1	0.3	1.4	1.4	0.9	0.9	1.5	0.1	1.2	0.5	1.0	0.6	1.2
Temruk port/30	1.5	0.3	0.1	0.4	0.8	0.7	1.5	1.1	1.4	1.0	0.7	0.6	2.8	0.6
Golubitskaya village/30	1.0	1.0	0.3	0.4	0.6	0.7	0.9	1.2	1.5	0.7	0.5	0.8	0.4	0.8
Port of Caucasus/29	7.1	2.1	0.2	2.4	0.8	1.0	1.3	1.3	0.9	1.0	1.1	2.4	0.2	2.4
Solovievskoe Girlo/29	1.4	1.2	0.3	0.2	0.6	0.8	0.8	0.7	1.2	0.8	0.6	0.8	0.2	0.8
Kulikovskoe Girlo/29	1.4	1.0	0.2	0.2	0.8	0.7	0.6	0.9	1.1	0.8	0.9	0.8	0.0	0.6
Perekopka village/29	1.6	0.9	0.2	0.2	0.6	0.6	0.5	0.5	1.1	0.8	0.8	0.6	0.0	0.6
Zozulievskoe Girlo/28	1.3	0.8	0.2	0.2	0.4	0.4	0.5	0.5	0.9	0.8	0.6	0.6	0.2	0.6
Taman village/27	2.6	2.1	0.5	1.8	2.4	1.3	1.2	1.2	0.9	1.0	1.0	2.6	0.6	1.8
Peresyp village/26	1.7	1.5	0.1	1.2	1.0	0.8	1.0	1.2	0.5	1.5	1.9	0.8	0.2	0.6
Primorsky village/26	1.5	1.2	0.5	0.8	1.0	0.7	1.1	1.8	1.3	1.0	0.2	1.6	0.4	1.0
Tuzla Spit (the Black Sea side)/25	3.0	2.0	0.5	1.4	0.6	0.5	0.8	1.6	0.5	1.2	1.9	1.4	0.0	2.4
Tuzla Spit (the Azov Sea side)/25	1.8	1.5	0.2	1.8	1.0	1.0	0.9	1.7	0.6	1.0	0.6	1.4	0.4	3.4
Panagia Cape/17	4.2	0.6	0.4	–	1.2	0.9	0.5	1.8	–	0.0	0.7	3.0	0.4	3.0
Bugazskaya Spit, the Western end/11	–	1.0	0.0	–	1.0	0.6	0.5	0.8	–	–	–	–	–	–

In order to determine dynamics of TPHs concentration of varying impact level, the Russian waters of the Azov and Black Seas jointly with the Kerch Strait up to the fairway were divided into 8 sections bearing in mind the baseline level of pollution and the trajectory of oil spilled during the Kerch Strait accident (Fig. 6.1.10d). Each of those zones had its own natural peculiarities of hydrological regime and water currents that were largely determined by their natural geo-formations being the islands, capes or spits.

Before 2007 and later, samples were occasionally collected in the Dinsky Bay and on the Azov Sea littoral to the North from the Temruk Bay. Therefore, no enough data to assess TPHs dynamics in the areas VI and VIII were present (Fig. 6.1.10d). At least 43 samples were collected in every of the rest of the areas (Fig. 6.1.10d). For example, the Temruk Bay was sampled 269 times (Table 6.1.10c) since the Kerch Strait accident.

The TPHs content seasonal dynamics in the Kerch Strait have demonstrated that pollution level was high during a short period of two months after the Kerch Strait accident

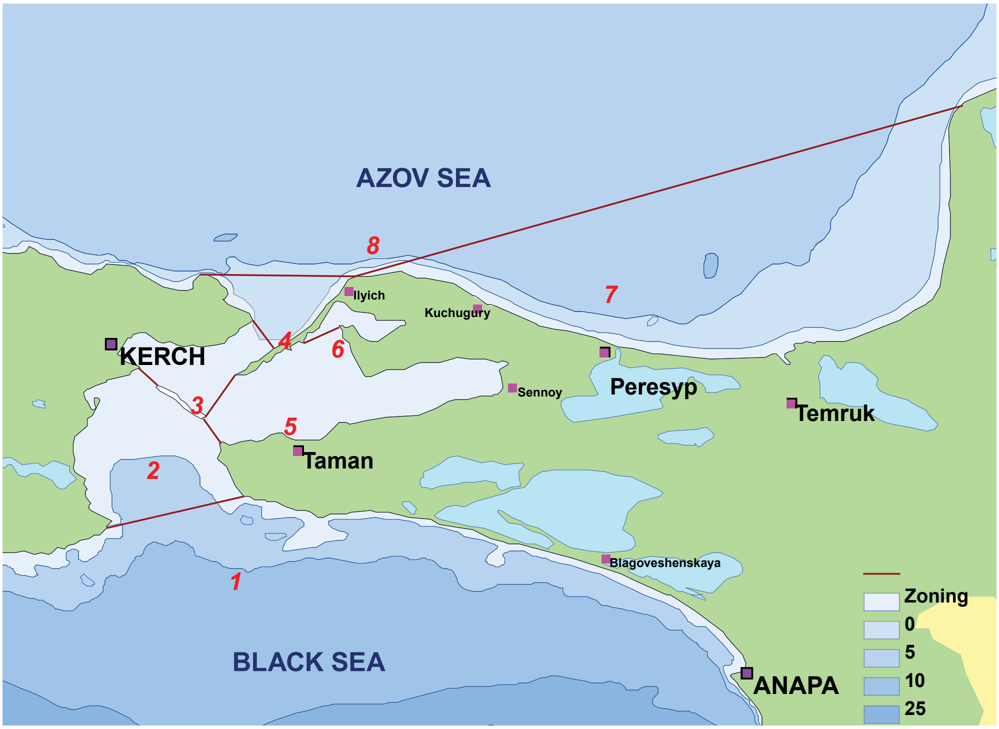

Fig. 6.1.10d. Zoning of the Kerch Strait and adjacent littorals of the Black and the Azov Seas: I — littoral of the Black Sea from the Kerch Strait till the Arkhipo-Osipovka village; II — the Kerch Strait Southern part (from the Tuzla Island to the Iron Horn Cape); III — the Kerch Strait central part (the water area of the Port of Caucasus); IV — the Kerch Strait Northern part (from the Port of Caucasus till the Ahilleon Cape); V — the Taman Bay; VI — the Dinsky Bay; VII — the Temruk Bay; VIII — the Azov Sea.

Table 6.1.10c. The number of samples collected by the Kuban EHMS at various sites of the Kerch Strait, the Azov and Black Seas in November 2008 — June 2009. TPHs content is presented as range of concentration and is given in mg/l and MAC, and the same is valid for the average parameters.

N	Location	Zone	The number of samples collected	Range: Min/Max	Average
1	The Black Sea littoral till the Arhipo-Osipovka village	I	57	≤0.02–0.80 (16 MAC)	0.04 (0.09 MAC)
2	The Kerch Strait Southern part (from the Tuzla Island till the Iron Horn Cape)	II	84	≤0.02–0.34 (6.9 MAC)	0.07 (1.4 MAC)
3	The Kerch Strait Central part (the water area of the Port of Caucasus)	III	86	≤0.19–1.7 (34 MAC, 13.11.2007)	0.07 (1.4 MAC)
4	The Kerch Strait Northern part (from the Port of Caucasus till the Ahilleon Cape)	IV	43	0.004 (0.08 MAC) — 2.5 (50 MAC, 13 November 2007)	0.15 (3 MAC)
5	The Taman Bay	V	61	0.18 (3.6 MAC, 17 November 2007)	0.06 (1.2 MAC)
6	The Dinsky Bay	VI	11		
7	The Temruk Bay	VII	269	0.64 mg/l (13 MAC, 15 November, 2007	0.05 (1 MAC)
8	The Azov Sea	VIII	6		

including its extreme levels in the first few days (Fig 6.1.10e). After that a substantial decrease of the Kerch Strait pollution level was recorded to vary within 1–2 MAC. The Kerch waters rather high TPHs content could be taken for the area as baseline parameter independent from the accident and oil spilled by *Volgoneft-139* in November 2007. In general, presence of other, relatively constant, TPHs sources in the Kerch Strait was possible: illegal discharges from the vessels, oil spills to occur while bunkering, as well as industrial, municipal, and storm discharges, etc. In the past, according to the monitoring data collected in the Kerch Strait Russian section, the TPHs average content was quite high reaching 0.073 mg/l (1.5 MAC) (Korshenko A. N. *et al.,* 2008). It is more likely that TPHs concentrations increased to up to 2 MAC in March 2008 and particularly in February 2009 were caused by other than related to the Kerch Strait 2007 accident factors.

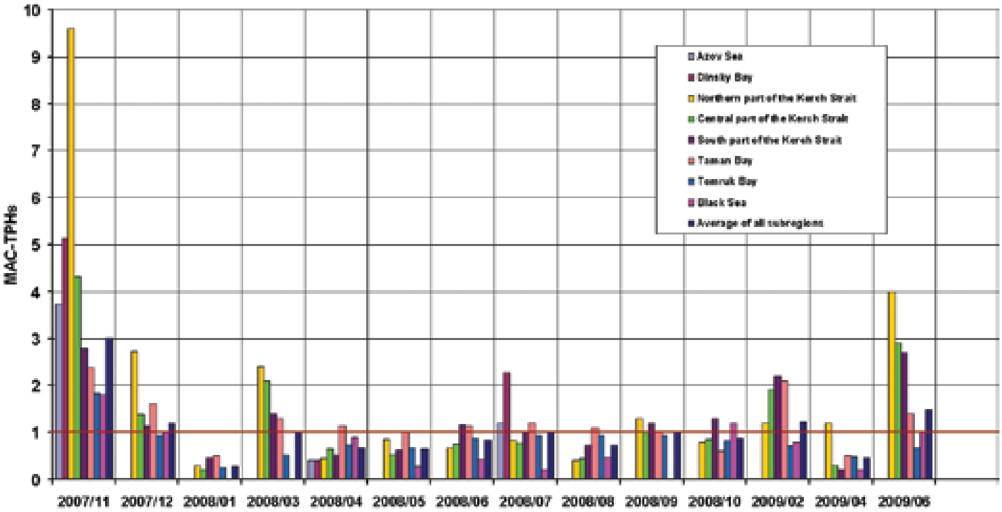

Fig. 6.1.10e. Seasonal dynamics of TPHs content (in MAC) in different zones of the Kerch Strait area in November 2007–June 2009.

Conclusions of the Roshydromet monitoring results

Analyses of monitoring data collected in the Kerch Strait area since November 2007 have resulted in the following conclusions: High levels of TPHs pollution were recorded practically in all the waters surveyed during a short period of two months immediately after the Kerch accident. Later, the level of pollution decreased significantly to reach the baseline concentrations of 1–2 MAC. It is likely that other constant sources of TPHs pollution were present in the area, such as illegal discharges from the vessels, oil spills to occur while bunkering, as well as industrial, municipal, and storm discharges, etc.

The Roshydromet monitoring program was not adapted to comprehensively study the short-term impact of an accident. It was rather focused on the long term permanent observations at specifically selected stations. As a result, irregular sampling only was carried out after the Kerch Strait accident in the areas of interest, and only part of polluted waters was studied, while very few surveys of the bottom waters (usually heavier polluted by hydrocarbons) were carried out. Besides, historical data on pollution of the Kerch Strait waters and its sediments were scarce due to the absence of regular observations in that particular area (Korshenko A. N, Panova A. I., 2009, 2009a).

Sampling of bottom sediments and benthic communities is essential for determining their contamination level, since they are the environmental 'memory' to record the chemical pollution negative impacts. The Roshydromet monitoring program lacked a biological component. Those gaps in observations impeded assessment of the long term petroleum impact on environment of the Black and Azov Seas, including the Kerch Strait.

6.1.11. RU: VNIRO. July 2008: The Kerch Strait and the Taman Bay

In July 2008, a complex oceanological expedition was conducted in the Kerch Strait and the Taman Bay, and it was organized by the All-Russian Fishery Institute (VNIRO, Moscow). In its course, hydrological and hydrochemical parameters were measured, and presence of petroleum and other chemical contaminants in the waters and bottom sediments was studied, while samples were collected at 38 stations. In the bottom layers at two stations (31st and 32nd, inner part of the Taman Bay at depth 5 m) the presence of heavy oil, probably related to the spillage from the *Volgoneft-139* tanker, was registered. At all other stations, neither in water nor in bottom sediments any petroleum was found.

6.1.12. RU: ChAD. Cruise observations in July, August, November and December 2008

The Black-Azov Seas Directorate of Rosprirodnadzor (ChAD, Novorossiysk) organized a post-disaster needs environment assessment after the Kerch Strait accident to cover the Black and Azov Seas impacted areas of the strait (Chapter 5.2). The total concentration of petroleum hydrocarbons (TPHs) was measured through applying a fluorometric method[1]. Their maximum concentration observed in July-December 2008 was recorded as 1.64 mg/l (33 MAC), while the average content was 0.04 mg/l (0.8 MAC) in the period under observation. TPHs distribution was very patchy and exhibited spots of high concentrations in the Kerch Strait various sections, where it was periodically exceeding the MAC value.

Petroleum hydrocarbons spatial variability on 24 July 2008

Petroleum hydrocarbons content varied from analytical zero to 1.635 mg/l (32.7 MAC) with the average of 0.046 mg/l (0.92 MAC). Also, 107 TPHs samples (64 %) taken had the concentration exceeding the analytical detection limit of 0.005 mg/l. Vertically, concentrations were unevenly distributed and were higher at the surface (Table 6.1.12a). The surface waters concentrations significantly differed from those in the bottom layer. In the surface waters two patches having a very high level of TPHs presence (about 33 MAC) were registered inside the Taman Bay area and at one of the North-Eastern stations near the Chushka Spit (Fig. 6.1.12a). Waters of the bottom layers were rather clean, and TPHs concentration near the Chushka Spit and inside the Taman Bay stood at 1 MAC. Up to 27 MAC concentrations were recorded in the Southern part of the Kerch Strait only.

Table 6.1.12a. Concentration of petroleum hydrocarbons (mg/l) in the surface and bottom waters of the Kerch Strait on 24 July 2008.

Layer	Range	Average	Impacted areas (from 1 to 33 MAC)
Surface	0–1.635 mg/l	0.097 mg/l (1.9 MAC)	The Taman Bay, the Chushka Spit Northern part
Bottom	0–1.345 mg/l	0.052 mg/l (1.0 MAC)	The Kerch Strait-Black Sea Southern part

[1] This method is based on extraction of hydrocarbons by chloroform from the samples for the extract further chromatographic purification after the change of dissolvent by hexane and with further measurement of fluorescence by the Fluorat-02 fluid analyzer.

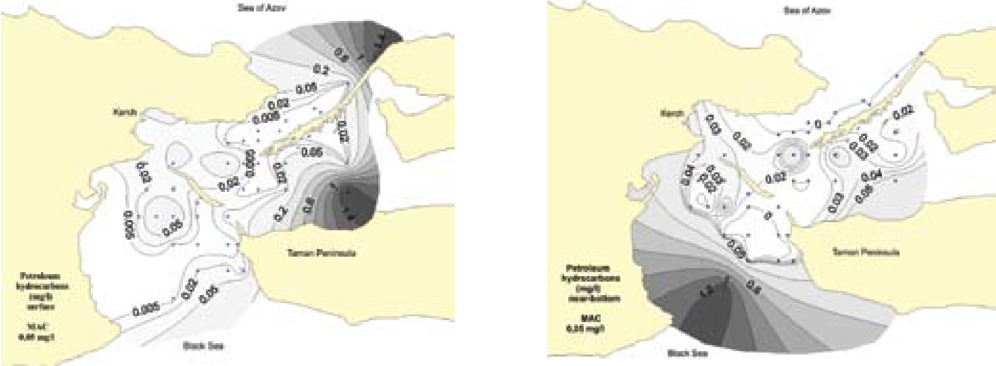

Fig. 6.1.12a. Total petroleum hydrocarbons concentration (mg/l) in the surface and near-bottom waters of the Kerch Strait on 24 July, 2008.

On 31 August, 2008

In August 2008, high TPHs concentration (3.2 MAC) was detected around the Tuzla Island, however levels at analytical zeros or close to 0.5 MAC were registered at the nearby stations (Table 6.1.12b, Fig. 6.1.12b). Vertically, TPHs distribution was rather even. Patches of relatively high TPHs concentrations (above 0.2 MAC) were detected in the Northern narrowness of the Kerch Strait and were most probably resulting from the land based sources. Average for the whole water column stood at 0.021 mg/l.

Table 6.1.12b. Concentration of petroleum hydrocarbons (mg/l) in the surface and bottom waters of the Kerch Strait on 31 August 2008.

Layer	Range	Average	Impacted areas (from 1 to 3 MAC)
Surface	0–0.160 mg/l	0.022 mg/l (0.4 MAC)	The Tuzla Island
Bottom	0–0.074 mg/l	0.021 mg/l (0.4 MAC)	Area between the Kerch port and the Port of Caucasus, Chushka Spit

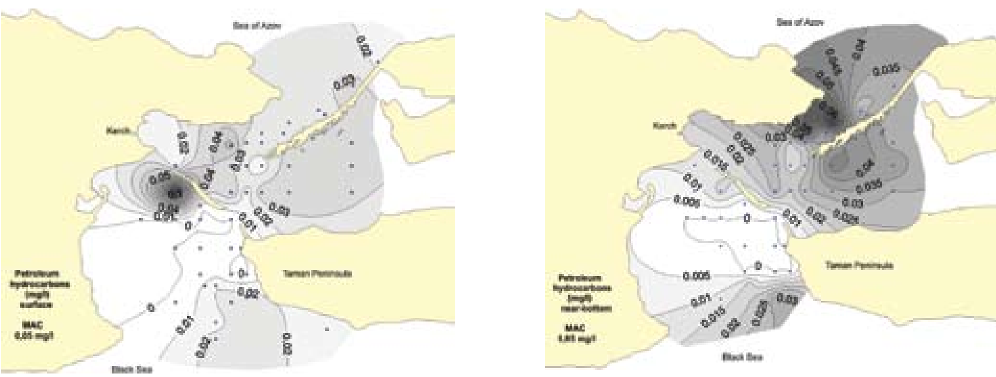

Fig. 6.1.12b. Total petroleum hydrocarbons concentration (mg/l) in the surface and near-bottom waters of the Kerch Strait on 31 August, 2008.

In November 2008

In autumn, 150 samples were collected and all of them had high petroleum content exceeding the analytical detection limit of 0.005 mg/l. Concentration varied from 0.0024 mg/l to 0.094 mg/l (0.021 mg/l in average). Levels exceeding MAC were registered in 9.3 % of all samples. TPHs concentrations of a baseline level were rather common for the area, while patchiness was more actively expressed in the bottom layers and a relatively high TPHs content was detected offshore the Panagia Cape, westward of the Tuzla Island, and in the Azov Sea (Table 6.1.12c, Fig. 6.1.12c).

Table 6.1.12c. Concentration of petroleum hydrocarbons (mg/l) in the surface and bottom waters of the Kerch Strait in November 2008.

Layer	Range	Average	Impacted areas (from 1 to 2 MAC)
Surface	0.004–0.094	0.019 mg/l (0.4 MAC)	The Northern narrowness
Bottom	0.002–0.070	0.024 mg/l (0.4 MAC)	Offshore the Panagia Cape, the Tuzla Island and the Azov Sea

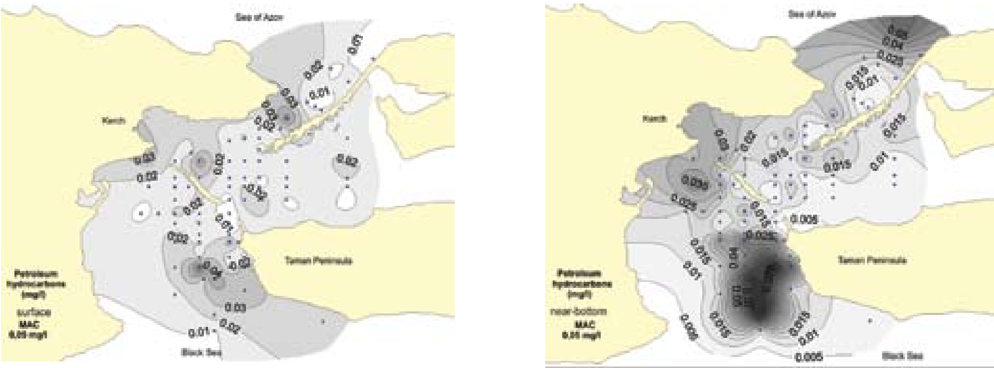

Fig. 6.1.12c. Total petroleum hydrocarbons concentration (mg/l) in the surface and near-bottom layers of the Kerch Strait on 6–15 November 2008.

In December 2008

TPHs concentrations exceeded 1 MAC in 23 % of all samples collected. The maximum concentration observed (1.1 mg/l) was reaching 22 MAC in the surface layers. Patchiness differed at the surface and at the bottom, while vertically TPHs distribution was uneven. (Table 6.1.12d, Fig. 6.1.12d).

Table 6.1.12d. Concentration of petroleum hydrocarbons (mg/l) in the surface and bottom waters of the Kerch Strait in December 2008.

Layer	Range	Average	Impacted areas (from 1 to 22 MAC)
Surface	0.006–1.100	0.098 (2.0 MAC)	The Kerch Strait Southern part
Bottom	0.006–0.269	0.034 mg/l (0.7 MAC)	The Kerch Strait Southern part

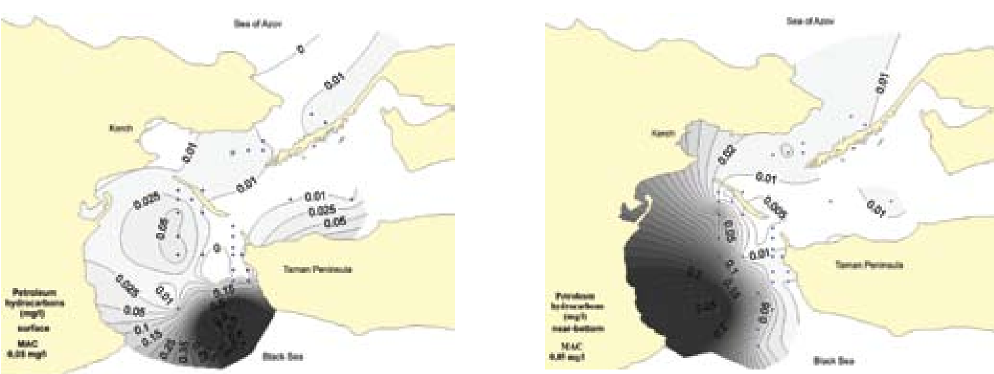

Fig. 6.1.12d. Total petroleum hydrocarbons concentration (mg/l) in the surface and near-bottom layers of the Kerch Strait in December 2008.

6.1.13. Summary: Presence of petroleum hydrocarbons in the water

The TPHs average concentration was quite stable and stood at the levels around 1.0 MAC (0.05 mg/l). It was demonstrated by the summary table of TPHs measurement data (Table 6.1.13a) obtained in the course of various expeditions organized in the framework of the Ukrainian routine monitoring program and in the result of the Roshydromet observations, as well as by all the mentioned above results of surveys over the Kerch Strait after the Kerch accident. Besides, the maximum concentration could significantly vary to occasionally exceed the High Level (HL) of pollution (1.5 mg/l) and even the Extremely High Level (EHL) of pollution (more than 2.5 mg/l), (Koshenko A. N. *et al.,* 2009). Such a strong variability has resulted out of TPHs patchy distribution both on the surface and in the water column.

The value of average concentrations observed has signaled that the Kerch Strait waters were kept chronically polluted by petroleum hydrocarbons during the last three decades, as well as during the two years to evolve after the Kerch Strait accident.

Low efficiency of existing monitoring systems became obvious when, in case of an accident, the probability to spot a drifting oil spill by means of fixed stations proved to be minimal. Routine observations make sense for trends assessment, but should be supplemented by samplings at the possible sources of contamination sites, i. e. along the routes of vessels, at the ports, close to the vessels at bunkering, in the areas of dredging and dumping, in transshipment areas, etc. Any method of remote observation could be extremely important and highly recommended in addition.

Table 6.1.13a. Total petroleum hydrocarbons concentrations (mg/l) in the Kerch Strait area marine waters.

	Period	Minimum	Maximum	Average	Position of the maximum patch	Expedition, organization
USSR/UA	1981–2007, USSR and Ukrainian Monitoring Data	–	2.96 (59 MAC), October 1982	–	the Kerch Strait, transect of the Crimea port and the Port of Caucasus	MB UHMI
UA	1992–2000, the Kerch Bight Monitoring	–	–	0.01–0.13	the Kerch Bight	YugNIRO
UA	2000–2007, the Kerch Bight Monitoring	–	–	0.04–0.28	the Kerch Bight	YugNIRO
UA	2007–2009, Ukrainian Monitoring Data	0.000	0.31 (6.2 MAC)	–	12 August 2008, close to the Port of Caucasus	MB UHMI
UA	21 November 2007	0.024	0.044 (0.9 MAC)	–	the Tuzla Island	YugNIRO
UA	9–17 December 2007	<0.05	0.019 (3.8 MAC)	–	the Tuzla Island	IBSS
UA	7 February 2007	–	~0.034 (0.7 MAC)	–	the Kerch Strait	YugNIRO
UA	End April 2007	–	0.219 (4.4 MAC)	–	the Kerch Strait	YugNIRO
UA	May April 2007	0.034	0.09 (1.8 MAC)	–	the Kerch Strait	YugNIRO
UA	15–22 November 2007	~0.04	0.10 (2.0 MAC)	–	the Kerch Bight,	YugNIRO
RU	13.11.2007–03.06.2009, Russian Monitoring Data	0.000	2.50 (50 MAC)	0.067	13 November 2007, the Chushka Spit	Kuban Estuarine Station
RU	July 2008	0.000	+	–	Entire part of the Taman Bay	VNIRO
RU	July 2008	0.000	1.635 (33 MAC)	0.046	Entire part of the Taman Bay	RosPrirod-Nadzor
RU	November 2008	0.002	0.094 (1.9 MAC)	0.021	the Black Sea	RosPrirod-Nadzor
RU	December 2008	0.006	1.100 (22 MAC)	0.066	the Black Sea	RosPrirod-Nadzor
UA	8 July 2009	0.02<	0.05 (1 MAC)	0.05	the Kerch Strait	UkrSCES
UA	December 2009	0.05<	0.05<	0.05<	Nearby the Tuzla Island	MHI and MB UHMI