Chapter 5. Standard hydrochemistry

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5.1. Background and baseline conditions observed in 1981–2007

In the former Soviet Union, standard hydrochemistry and pollution level investigations in the waters of the Kerch Strait were carried out regularly in the period 1981–1992 in the framework of the state monitoring of marine waters[1] by the HMS «Opasnoe», situated in the vicinity of the city of Kerch. Since 1992 the monitoring has been sustained by Ukraine in the framework of its Hydrometeorological Service (the same HMS «Opasnoe»). The program covers determination of concentrations of dissolved oxygen (O_2), pH, alkalinity (Alk), phosphates ($P\text{-}PO_4$) and total phosphorus (P_{total}), silicates (Si), nitrites ($N\text{-}NO_2$), nitrates ($N\text{-}NO_3$), ammonia ($N\text{-}NH_4$), and a number of pollutants such as total petroleum hydrocarbons (TPHs), detergents (Det) and phenols (Phen). The quantity of measurements performed per environmental parameter in 1981–2007 is presented in Table 5.1a.

Table 5.1a. The number of measurements of standard hydrochemical parameters and some pollutants at transect between ports Crimea and Caucasus in 1981–2007.

Year	O_2	ph	Alk	PO_4	P_{total}	Si	NO_2	NO_3	NH_4	TPHs	Det	Phen
1981	251	213	190	171	12	169	171	-	-	150	137	-
1982	133	114	133	133	-	133	133	-	-	24	64	-
1983	295	196	190	183	-	171	172	34	-	42	91	-
1984	239	229	124	122	-	122	122	98	-	137	96	-
1985	178	120	83	83	-	83	83	83	-	125	82	-
1986	260	260	70	70	70	70	70	70	-	28	56	-
1987	52	52	52	43	43	43	36	36	-	-	-	40
1989	410	423	60	60	60	60	60	60	60	71	8	58
1992	250	250	96	96	96	96	96	96	96	126	92	94
1994	48	48	48	48	48	48	48	48	48	48	48	48
1995	24	24	24	24	24	24	24	24	24	24	24	24
1997	60	60	60	60	60	60	60	60	60	60	60	60
1998	48	48	48	48	48	48	48	48	48	48	48	48
1999	48	48	48	48	48	48	48	48	48	48	48	48
2000	56	56	56	56	56	56	56	56	56	56	56	56
2001	48	48	48	48	48	48	48	48	48	48	48	48
2002	104	104	104	104	104	104	104	104	104	104	104	104
2003	192	192	192	192	192	192	192	192	192	168	176	184
2004	279	279	279	279	279	279	279	279	279	168	232	216
2005	200	200	200	200	200	200	200	200	200	200	200	200
2006	200	200	200	200	200	200	200	200	200	200	200	200
2007	200	200	200	200	200	200	200	200	200	200	200	200
Total	3575	3364	2505	2468	1788	2454	2450	1984	1663	2075	2070	1628

Detergents. Since 1981, during all periods of monitoring the waters of the Kerch Strait were rather clean from detergents. Meanwhile, spring and autumn were the seasons of a visible increase in the detergents content in the area (Fig. 5.1a). The maximum observed was 8.4 MAC (840 µg/l) in May 1983.

Phenols. The mean concentrations of phenols observed were generally less than 3 µg/l, with isolated cases of high phenols content in the waters of the narrowest place of the Kerch Strait. A very high level of 20 MAC (20 µg/l) was recorded in December 1990.

[1] The routine monitoring system in the framework of the Hydrometeorological Service does not include sampling of sediments and biota. This is valid for both the former USSR system and present Ukrainian and Russian systems.

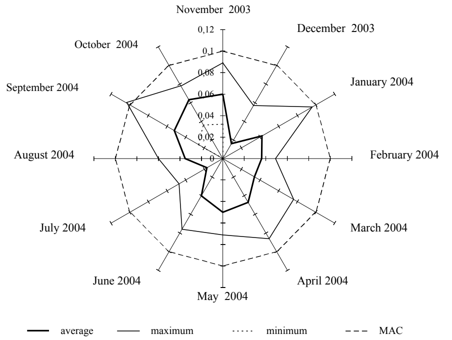

Fig. 5.1a. Seasonal distribution of detergents (mg/l) in the Kerch Strait waters in 2003–2004.

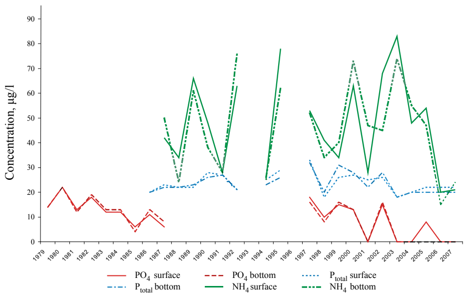

Fig. 5.1b. Average nutrients annual dynamics in the Kerch Strait waters in 1979–2007.

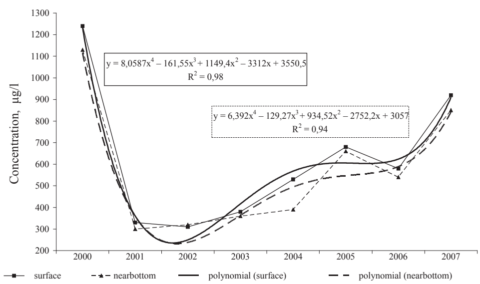

Fig. 5.1c. Approximation of the total nitrogen concentration dynamics in the Kerch Strait waters in 2000–2007.

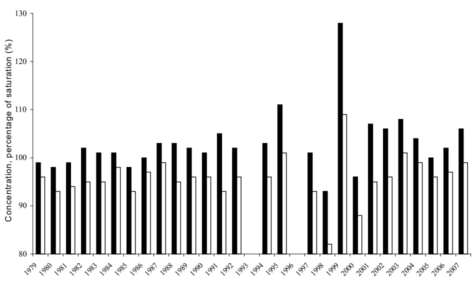

Fig. 5.1d. Average dissolved oxygen concentration (% of saturation) in surface (black) and bottom waters (white) of the Kerch Strait in 1979–2007.

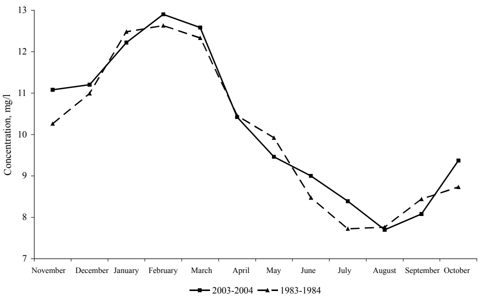

Fig. 5.1e. Seasonal variability of oxygen concentrations (mg/l) in the Kerch Strait waters in 1983–1984 and 2003–2004.

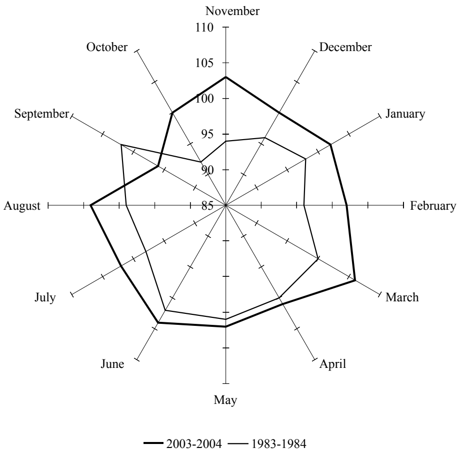

Fig. 5.1f. Seasonal distribution of oxygen saturation (%) in 1983–1984 and 2003–2004.

Nutrients (Fig. 5.1b). Average annual concentrations of phosphates exceeded the level of detection limit DL (10 μg/l) in the first half of 1980s and at the end of 1990s only. The maximum reached was 76 μg/l in 1980. The maximum total phosphorus content was recorded in bottom waters in September 2003 — 160 μg/l, a value which is half the ecological norm of 300 μg/l[2].

The mean concentrations of ammonia never exceeded the MAC of 390 μg/l and the maximum in surface waters was 950 μg/l in March 2004. Nitrites content usually was below the DL of 5 μg/l, however, in June 2007 it reached 47 μg/l (2.4 MAC) in the surface layer. The total nitrogen concentration varied from 37 μg/l in April 2004 to 2840 μg/l in July 2000. For the period of 2000–2007 this parameter showed a strong inter-annual variability (Fig. 5.1c) with an increasing tendency since 2002.

Oxygen. Over the whole period of monitoring the waters in the Kerch Strait were well aerated at surface as well as in the near bottom layers (Fig. 5.1d). Only in a single case, in June 1991, in the narrowest part of the Strait the oxygen in the near bottom layer dropped down to 2.96 mg/l (39 % of saturation).

Seasonally high oxygen concentrations were observed during winters and they were decreasing closer to summer as examples of the 1983–1984 and 2003–2004 periods demonstrate (Fig. 5.1e, f).

[2] Note: This standard is the accepted in Ukraine. The BSC lobbies for changes of standards and making them more stringent. The proposed standard for TP is 100 μg/l.

IWP. The complex Index of Water Pollution (see Chapter 7 for description of the index), calculated for the concentrations of three priority pollutants of the Kerch Strait area (petroleum hydrocarbons, detergents, ammonia) and oxygen content evidenced good water quality in the period 2003–2006, however, shortly before the Kerch accident the waters were classified as 'moderately polluted' (Tab. 5.1b).

Table 5.1b. The concentration of main pollutants and level of IWP in the Kerch Strait waters in 2003–2007.

Parameter	Mean concentration in MAC				
	2003	2004	2005	2006	April–October 2007
TPHs	1.6	1.6	1.2	1.2	2.0
Detergents	0.43	0.47	0.62	0.37	0.48
Ammonia	0.21	0.11	0.14	0.04	0.06
Oxygen	0.70	0.67	0.72	0.69	0.72
IWP	0.74	0.71	0.67	0.68	0.82
Class	II	II	II	II	III
Water quality	clean	clean	clean	clean	moderately polluted

5.2. Observations conducted in 2007–2009 to study the effect of the Kerch accident

Six major Russian and Ukrainian Scientific Research Institutes got involved in the investigations on the Kerch accident effects in 2008–2009 in terms of hydrochemical regime change: the SB SIO RAS, AzNIIRKH, SSC RAS, MHI, MB UHMI and UkrSCES. Regular observations in the Kerch Strait continued also in the frames of the Ukrainian National Monitoring Program (HMS Opasnoe). All observations organized in the Kerch area in 2008–2009 are described further.

5.2.1. ChAD (Russia): Expeditions in July, August, November and December 2008

In 2008 four cruises were carried out in July-August, November, and December by the Black-Azov Seas Directorate of Rosprirodnadzor (ChAD, Novorossiysk). The aim of these complex investigations was to assess the state of the marine environment in the Kerch Strait, Black and Azov Seas, and especially at the places of shipwrecks of the Kerch accident. Data on dissolved gases, concentrations and distribution of inorganic nutrients and organic matter in water and sediments, contamination by petroleum hydrocarbons and sulfur, and other environment parameters were collected during the expeditions at 77 stations (Table 5.2.1a, Fig. 5.2.1a). Laboratory and analytical work was conducted at the SB SIO RAS in Gelendzhik. Samples collection, processing, and analysis were performed using standard oceanographic methods (Oradovsky S. G., 1993, Bordovsky O. K., Chernjakova A. M., 1992).

Table 5.2.1a. Hydrochemical parameters of water and bottom sediments investigated by ChAD in the area of the Kerch Strait during July–December 2008.

N	Measured parameters	Number of Samples	
		Water	Bottom Sediments
1	Salinity	92	–
2	pH	377	–
3	Suspended matter	155	–
4	Dissolved oxygen	274	–
5	Oxygen, % of saturation	274	–

6	Ammonia	200	–
7	Nitrites	200	–
8	Nitrates	191	–
9	Silicates	194	–
10	Phosphates	199	–
11	Petroleum hydrocarbons	378	154
12	Sulphur (S)	–	150

Salinity. The distribution of salinity in the Kerch Strait is defined by the interaction between saline waters of the Black Sea and less saline waters of the Azov Sea. As a result, salinity decreases in the Strait from the South to the North (Fig. 5.2.1b). Salinity variability is very high and depends on the hydro-meteorological conditions in the Strait. In 2008 salinity varied in the range of 6.56–18.17 PSU. The average salinity was 15.01 PSU well corresponding to the long-term values known for the area (see Sub-chapter 3.5).

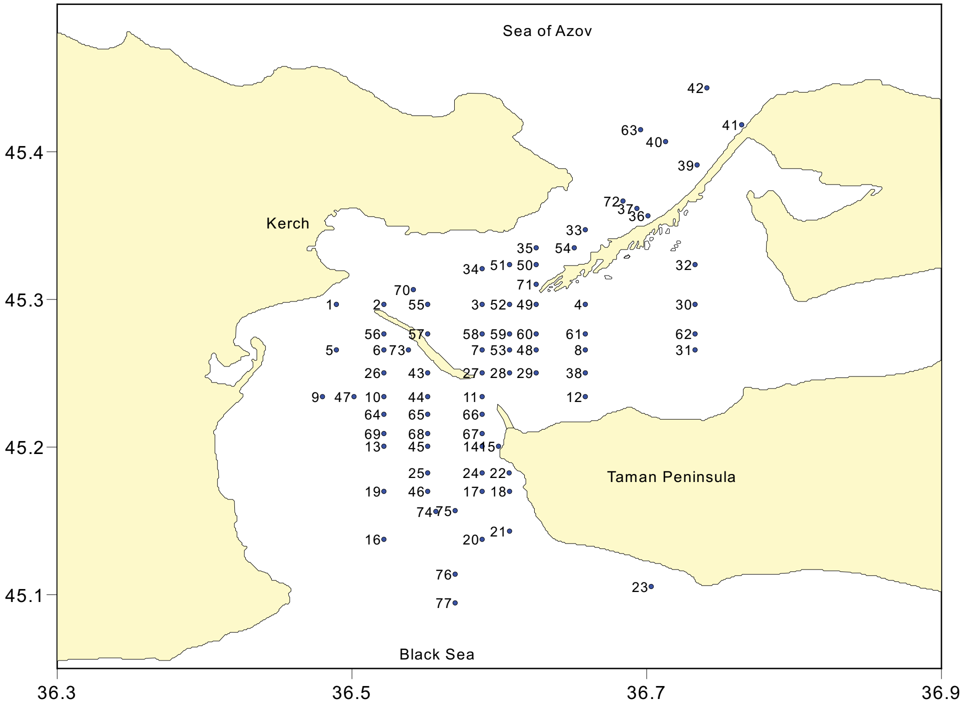

Fig. 5.2.1a. Location of stations in the Kerch Strait during July–December 2008.

Oxygen. Oxygen content varied from 5.79 mg/l to 12.11 mg/l (Fig. 5.2.1c) during the observation period, the average was 8.2 mg/l. The maximum oxygen saturation was 150 %, the average — 109 %, at some stations oxygen deficiency was observed. Mainly, it was due to predomination of decomposition over production because of an active decay of organic matter and respiration of organisms, and well related with the level of eutrophication/pollution in the areas of concern. For instance, in August 2008 the values around of Minimum Allowed Concentration (1 MinAC equal 6.0 mg/l, MAC List, 1999) were observed in bottom layers near the Panagia and Enikale Capes, 5.79 mg/l and 6.03 mg/l respectively, evidencing lower water quality. Hence, high concentrations of nitrate nitrogen and oil products were observed in water and

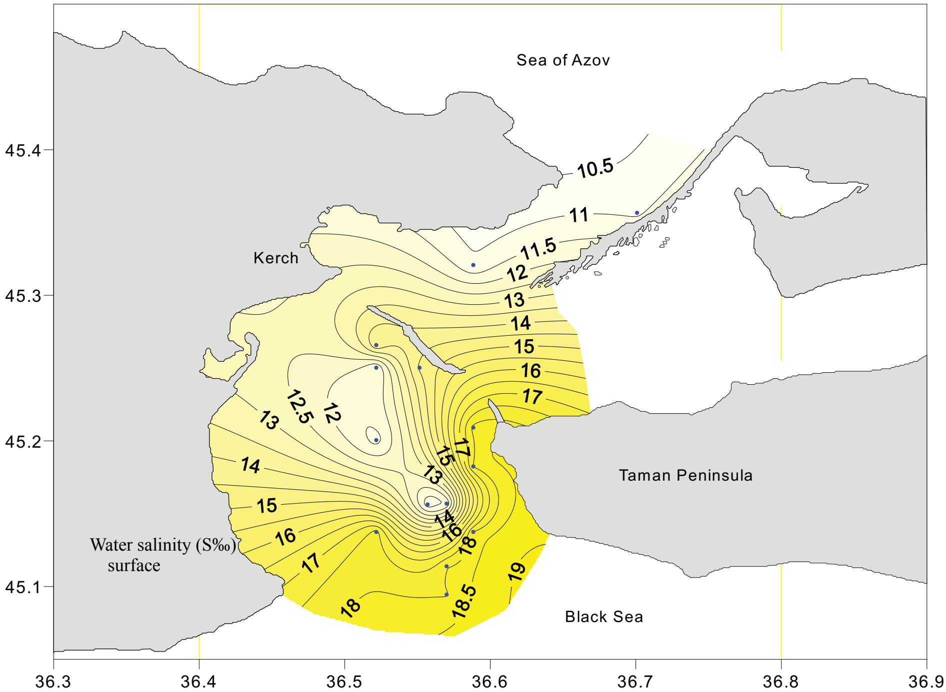

Fig. 5.2.1b. Water salinity (S‰) in the surface layer in December 2008.

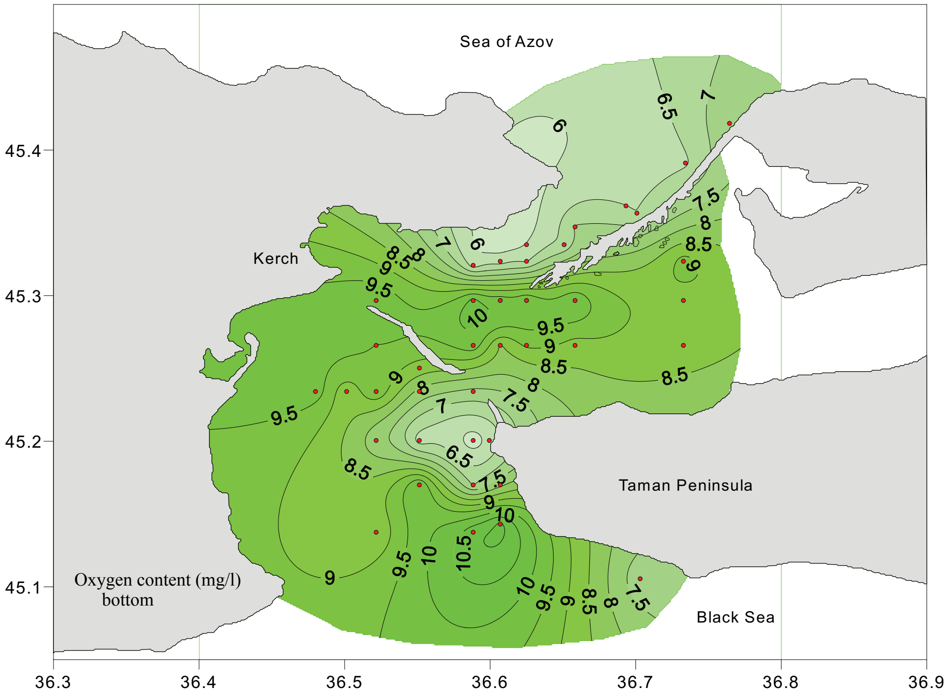

Fig. 5.2.1c. Oxygen content (mg/l) in bottom layers observed on 31 August, 2008.

bottom sediments at these two stations. Normal background concentrations, fluctuating around the average of 118 % of oxygen saturation, were observed at the rest of the studied stations in August.

There were no anomalies of oxygen content observed in November 2008. The oxygen concentration varied from minimum of 9.06 mg/l to maximum of 11.46 mg/l and the saturation varied from 99 % to 125 %. In December the minimum oxygen concentration of 9.72 mg/l was observed again near the Panagia Cape. In general, the oxygen content increased simultaneously with temperature decreasing during the observation period. The average content was 10.12 mg/l in November and 11.17 mg/l in December. However, the oxygen saturation decreased slightly to the averages of 107 % in autumn and 98.3 % in winter due to less intensive photosynthetic activity.

pH. This parameter varied from 6.66 to 9.05. Its maximum was observed in surface waters in summer time. The average value was 8.42. Low pH values were observed at the Panagia Cape and the Caucasus Port during the autumn expedition. As the norm for pH established from 6.5 to 8.5, the maximum observed pH values in the Kerch Strait were slightly over it in 2008 (1.06 of MAC for the maximum pH recorded), (MAC List, 1999). These high pH values were well related to the high water temperature and active photosynthesis processes, and they are natural during summers for this areas though exceeding established MAC.

Phosphates (P–PO_4). Phosphates content varied from 1 µg/l to 70 µg/l at the area observed. The values did not exceed MAC (150 µg/l). The average content was 8 µg/l. Maximal concentrations of phosphates were mostly discovered at the stations in the Northern part of the Strait, between the Enikale Cape and the Chushka Spit (Fig. 5.2.1d).

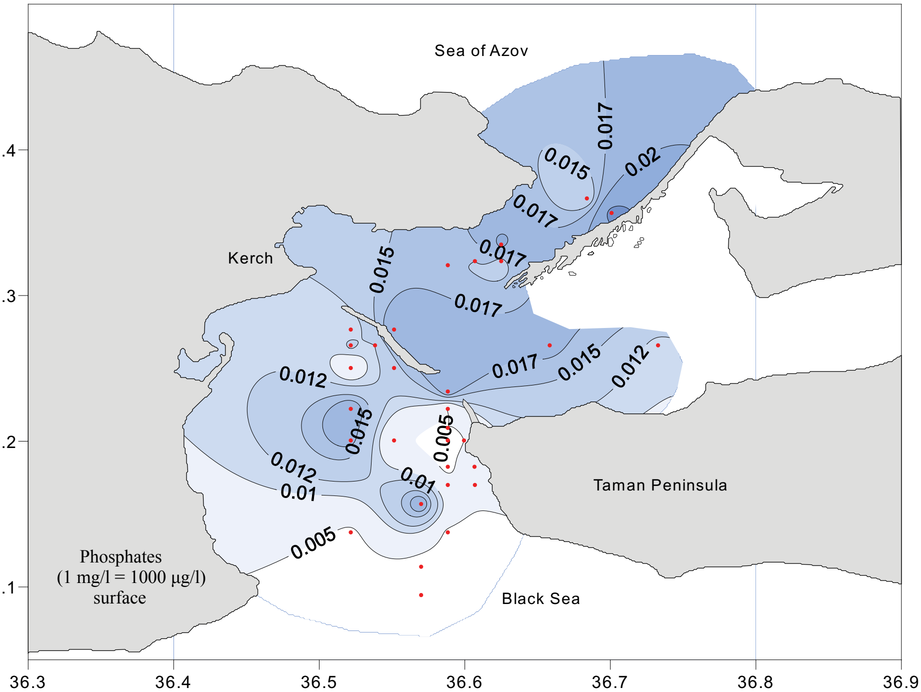

Fig. 5.2.1d. Phosphates concentration (mg/l) on the surface in December 2008.

The highest content of inorganic phosphorus was identified during winter time, when the average value was 12 μg/l. Maximum and average concentrations were two-fold higher in the Kerch Strait compared to the North-Eastern part of the Black Sea (Simonov A. I., Altman E. N., 1991).

Nitrites nitrogen ($N–NO_2$). In the summer cruises, nitrites were discovered in the Northern part of the Strait only, similarly to phosphates, between the Crimea and the Chushka Spit. This water area should be categorized as the most polluted. Nitrites appeared in other areas during autumn and winter, increasing in time. The concentrations in water varied from analytical zero to 15 μg/l. The average content was 1.6 μg/l. Vertically the content was higher in bottom layers. The values of nitrites were lower than the MAC for fisheries (80 μg/l) during the whole observation period.

Nitrates nitrogen ($N–NO_3$). Nitrates nitrogen content varied from 2 μg/l to 434 μg/l. The average value for July–December was 30 μg/l. In August, November, and December the averages were 14 μg/l, 24 μg/l and 56 μg/l correspondingly. The nitrates were substantially exceeding the background concentrations in November 2008 only. Maximal values were found at the Chushka Spit, Tuzla Island, and also around the Taman Peninsula. The nitrates content was increasing from summer to winter. The concentrations of nitrates were significantly higher in the Kerch Strait compared to the Black Sea.

Ammonium nitrogen ($N–NH_4$). The high content of ammonium nitrogen was the distinguishing feature for the studied area during the whole period of observations. Maximal values were recorded at the stations close to the Panagia Cape, Tuzla Island and Chushka Spit. The ammonia varied from 8 μg/l to 180 μg/l, with the average of 58 μg/l. The values were 4.4 times higher than those observed in the area of the Novorossiysk Port in 2008. The ammonia content can fluctuate significantly due to pollutions and processes related to biochemical decomposition of organic substances. Vertically, the content observed in surface layers was higher than nearby sea bottom. In time maximal values were observed in winter in parallel with increase in organic substances in water. Ammonia content did not exceed the MAC for fishery (2900 μg/l) in the studied area.

Silicates ($Si-SiO_4$). Silicates content varied from 1 μg/l to 1242 μg/l, with an average of 256 μg/l. MAC of Silica acid for fisheries is 1000 μg/l. The concentration of silicates at 3 stations was higher than norm and the maximum was 1.2 of MAC. The observed patch appeared due to water inflow from the Azov Sea enriched with dissolved silicate.

Suspended matters. The quantity of suspended matter varied from the level of detection limit of 1.0 mg/l to 399 mg/l. The average concentration of suspended solids was 31.6 mg/l (Fig. 5.2.1e). In general the content of SS was high in the whole water column in the Kerch Strait during the survey periods.

In adjacent Black Sea coastal waters the average concentration of suspended matter varied from 4 mg/l to 6 mg/l, which was several times lower than the regularly observed values in the area of the Strait. As a rule, maximum content in the water column is observed in the Southern and Northern parts of the Strait and nearby the Tuzla Island. During the 2008 summer and autumn surveys the average content of suspended matter was of 21.0 mg/l. It doubled almost twice (up to 47.5 mg/l) in winter. Usually, the suspended matter content is higher in the bottom layer. The major sources of suspended solids are the river flows, precipitation, and atmospheric deposition. In addition, turbulence dur-

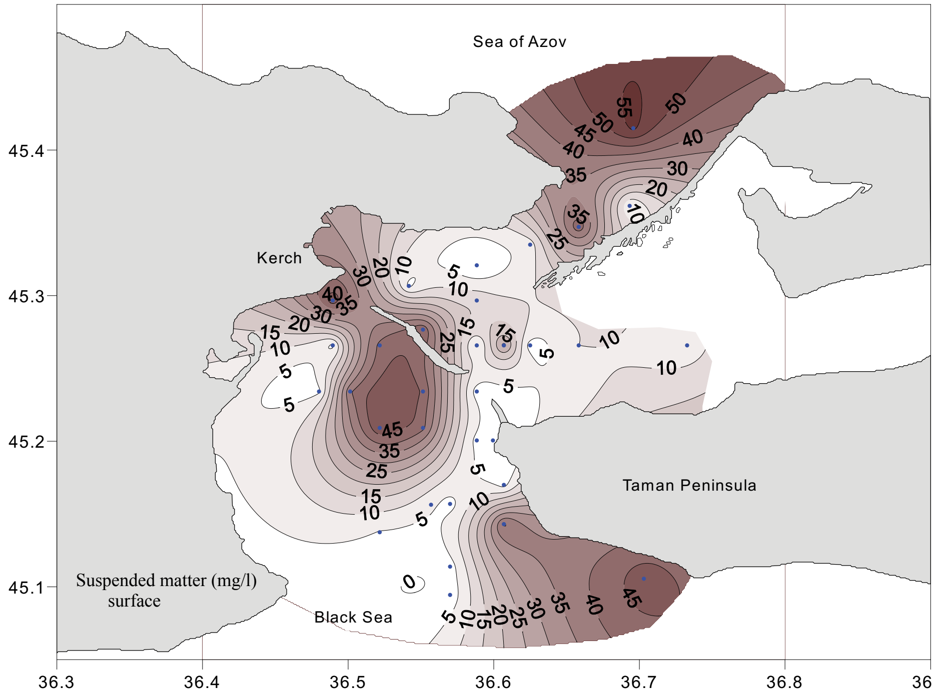

Fig. 5.2.1e. Content of suspended matter (mg/l) in the surface layer of the Kerch Strait in November 2008.

ing storms and intensive navigation increases the input of suspended matter from sediments to the shallow waters of the Kerch Strait.

Conclusions on the ChAD expeditions in 2008

The hydrochemical parameters of the shallow waters in the Kerch Strait significantly differ in values from those of the adjacent areas of the Black Sea. This difference is reflected, as a rule, in a higher content of nutrients and pollution, especially for areas close to the shoreline. Actually, the whole Kerch Strait is under a strong anthropogenic pressure, well reflected in persistently observed abnormal values of environment parameters.

The 2008 surveys in the Kerch Strait provided up-to-date information on the content and distribution of major hydrochemical parameters. The waters in the Strait were well saturated with oxygen; no hypoxic or anoxic situations were registered. However, there were areas with relatively low content of oxygen in bottom layers, and over-saturation at surface indicating active photosynthesis, hence high concentrations of nutrients and organic matter in the water. True, nutrients, suspended matter and pollutants in the Kerch Strait are higher than in the North-Eastern part of the Black Sea, and even higher than in the Gelendzhik and Cemes Bays which are characterized by limited water exchange and heavy anthropogenic impact. The most impacted areas in the Kerch Strait are situated between the Chushka Spit and Crimea shoreline, the section of the Taman Peninsula between the Panagia and Tuzla Capes, and the water area at the South side of the Tuzla Island. Despite of the high variability of hydrochemicals distribution in the Strait related to the complicated dynamics of water flows here, the high baseline concentrations of nutrients are quite stable in these waters and well related to external land-based or ship-borne sources. However, nutrients in 2008 were lower than MACs for fisheries. As per today, the hydrochemical regime of the Kerch Strait corresponds to the established standards of the Russian Federation. However, these standards (especially for nutrients) need serious revision, as they indicate values which are more suitable for fresh waters, and if observed in marine environment might cause serious disturbance to biota.

5.2.2. Opasnoe HMS (Ukraine): routine monitoring in 2008–2009

In the frames of the routine Ukrainian national monitoring of marine waters standard hydrochemical parameters were studied in the Northern narrow pass of the Kerch Strait at a transect between the ports of Crimea and Caucasus (Fig. 1a). The investigations were carried out from April to November 2008 and from April to June 2009 by the Opasnoe HMS during 35 field expeditions. Concentrations of dissolved oxygen, hydrogen ion (pH), general alkalinity, phosphates and total phosphorus, silicates, nitrites, nitrates, ammonia and total nitrogen, detergents, phenols and petroleum hydrocarbons were measured in 280 samples. The total petroleum hydrocarbons distribution is discussed in Chapter 6.

Detergents. In 2008 their concentrations varied from zero to 130 μg/l in surface waters with the average value of 38 μg/l, and from 0 to 83 μg/l in the near-bottom layer with a mean less than the detection limit of 25 μg/l. The maximum reached 1.3 MAC and was recorded at the Light Cape in September. In 4 samples only the detergents were above 1 MAC. In the first half of 2009, in eight samples only the concentrations were above the detection limit.

Phenols. In 2008 the range of phenols concentration was 0–3 μg/l. Elevated level was observed over the whole studied period. The monthly average concentration was similar to previous data collected in 2007. In the first half of 2009 phenols occasionally reached 4 μg/l in April and June, otherwise the mean value was less than 3 μg/l.

Nitrogen. Nitrites nitrogen ($N\text{-}NO_2$) was rarely found in May-October 2008, with concentrations changing within the range from below the detection limit of 5 μg/l to the maximum of 16 μg/l (surface waters in September 2008). Nitrates ($N\text{-}NO_3$) reached the level of 53 μg/l on 26 May in surface waters near the Crimea shore. Periodically in April-July, their concentration was below the detection limit of 10 μg/l. Ammonia was presented in the Strait waters permanently in the range of 0–104 μg/l. Its maximum was detected on 4 June 2008 near Crimea. The total nitrogen concentration varied between 130 and 980 μg/l, and its mean in the surface layer was 530 μg/l, whereas in near-bottom waters — 500 μg/l. In 2008, the Russian ecological norm of 500 μg/l was exceeded occasionally in April-July (e. g. on 23 April, 14 May, 4 June, 17 July), and frequently in August, September and October. In April-June 2009 the mean ammonia concentration was lower — 13 μg/l (compared to the average of 17 μg/l observed in April-June 2008). For total nitrogen the decrease was about 1.5 times, while for nitrites and nitrates remained in 2009 the same as 2008.

Phosphorus. In 2008 the concentration of inorganic phosphorus ($P\text{-}PO_4$) reached its maximum of 25 μg/l on 30 October in the surface layer and was below the detection limit (DL) of 10 μg/l in most cases observed within the warm period of the year from May to November. Monthly mean value exceeded DL only in September — 14 μg/l. The total phosphorus maximum was 42 μg/l, the averages were 24 μg/l and 22 μg/l in surface and bottom layers correspondingly. All values observed were significantly lower than the ecological norm of 300 μg/l. In 2009, the distribution and level of phosphorus remained unchanged compared to 2008.

Silicates. In 2008 the silicates concentration varied in the range of 10–1250 µg/l. The maximum was recorded on 24 September in surface waters. The mean value for similar seasons was 180 µg/l, and it slightly increased in 2009 to 220 µg/l.

Oxygen. The waters of the Kerch Strait were well aerated in 2008–2009. The oxygen saturation varied from 79% to 121% and the mean value was 90%. In all samples the oxygen content exceeded the ecological norm of 6 mg/l (set for the warm period of the year).

pH. In 2008 pH varied in the range of 7.31–8.60. The mean values for surface (8.42) and deep waters (8.38) were very close. In 2009 pH slightly decreased to 8.28 in both layers.

Index of Water Pollution (IWP). The Kerch Strait Index of Water Pollution based on the annual mean concentrations of petroleum hydrocarbons, detergents, ammonia and oxygen was calculated for 2008 at the level of 0.39, which allowed to qualify the waters in the strait as «Clean». In 2009 the IWP slightly increased to 0.52, however, the water quality class remained the same — «Clean» (see Sub-chapter 7.6 for details on IWP).

Conclusions on the UA monitoring

The UA monitoring data collected at a transect between the ports of Crimea and Caucasus show, in general, low level of nutrients and pollutants present in 2008 and first half of 2009. The mean concentrations of all measured parameters were lower than 1 MAC except for the total nitrogen. In 2008, the detergents content in the water decreased by up to 2.7 times compared to 2007, while the phenols level remained unchanged. The 2008 concentrations of total nitrogen and silicates were also lower than in 2007, and there was no significant change for other species of nutrients. The oxygen regime was rather good and had a negligible variation in both layers. The worse water quality according to measured concentrations was in the area close to the port of Crimea. According to the Index of Water Pollution, in 2008 the water of the Kerch Strait became less polluted and could be qualified as «clean» (IWP=0.39). In 2007 (IWP=0.82) it was classified as moderately polluted, as mentioned in Subchapter 5.1. In 2009, the waters were still «clean» even IWP slightly increased to 0.52.

5.2.3. AzNIIRKH (Russia): November 2007, April–October 2008

Expedition of AzNIIRKH to the Southern part of the Azov Sea was undertaken from 30 November to 3 December and to the Black Sea — from 6 to 7 December 2007. There were 12 radial cross sections with the center at the shipwreck of the *Volgoneft-139* tanker studied. The objectives of the studies in the Kerch Strait and in the Azov and the Black Seas were to identify: (i) boundaries in water and sediments of the spots polluted by oil and sulfur, and (ii) impact assessment on communities of aquatic organisms and environment, in general. Hydrological (salinity, flow velocity and directions, water temperature, waves, turbidity, and depth), standard hydrochemical and geological investigations were carried out in parallel. The following hydrochemical parameters were observed: dissolved oxygen, BOD_1, mineral and total phosphorus, ammonia, nitrites, nitrates, total nitrogen, silicates, dissolved matter and suspended solids, sulphates in the place as well as geochemical parameters (granulometry, pH, Eh, organic carbon and sulphates in the water).

Investigations on pollution included TPHs, PAHs and aliphatic hydrocarbons (C_{14}–C_{23}) in water and sediments. Studies on biota consisted of TPHs and PAHs in moluscs measurements, microbiological, hydrobiological and toxicological researches. Floating oil films, areas of high turbidity, foam and etc. were fixed visually with photo and video equipment. The size and location (coordinates) of the oil films were identified. The study area was limited to the range of the pollution after the Kerch shipwreck. The distance between stations was 10 miles (Fig. 5.2.3a). Water samples were collected at 3 to 5 layers depending on the depth of the area studied.

The highest concentrations of inorganic and organic nutrients were recorded in the North-Eastern part in the Taman Bay and South-West of the Kerch Strait. For the Taman Bay, the usual concentrations of ammonia was 110 µg/l, nitrites — 15 µg/l, nitrates — 65 µg/l, phosphates up to 35 µg/l (Fig. 5.2.3b–e). In the Kerch Strait nitrates were about 20–30 µg/l, phosphates 35–40 µg/l. Further, extreme concentrations of nutrients, such as the observed 260 µg/l of ammonia or 20 µg/l of nitrites were rare in the Strait (Fig. 5.2.3b, c).

The spatial distribution of N_{org} resembled the inorganic nutrients variability in space — higher concentrations allocated in the North and South-West parts of the Strait (Table 5.2.3a). Hence, in the Kerch Strait and the surrounding parts of the Azov Sea the present N_{org} was higher than in the Black Sea.

Table 5.2.3a. Concentration of organic nitrogen (N_{org}, µg/l) in the Kerch Strait and the Black Sea in the period of 30.11–07.12.2007.

Range of Norg (µg/l)/Area	Kerch Strait			Black Sea
	Taman Bay	Central	South-West	
Surface	260–380	180–270	330–370	190–250
Bottom	260–360	190–320	440–590	130–290

In average, content of the nutrients in the Kerch Strait was 1.5–2 times higher than those in the Black Sea. The same was discovered in the Azov Sea for ammonia and phosphates only (Table 5.2.3b).

Table 5.2.3b. Average nutrients concentrations (µg/l, above) and their range (below) in the surface and near bottom waters of the Kerch Strait region in the period of 30.11–07.12.2007.

Area	Ammonia		Nitrites		Nitrates		Phosphates	
	surface	bottom	surface	bottom	surface	bottom	surface	bottom
Azov Sea	34 16–62	35 16–78	7.3 2.5–14	7 2.6–12	23 5–79	19 5–58	13 9–43	13 6–49
Kerch Strait	68 32–260	46 25–100	6.4 0.5–10.7	8.3 0.8–21	19 7–62	20 9–65	17 11–28	24 13–41
Black Sea	29 27–33	31 27–34	6.5 6–6.9	6.4 5.6–7.3	7.1 5–10	8.1 6–14	11 6–17	14 9–18

Statistical data (collected on 30 November–7 December) processed through the multiple correlation method allowed to identify — with high degree of probability — the Kerch shipwreck impact on two polluted spots (areas I and II on Fig. 5.2.3g respectively), (R = 0.75–0.99). One of them was located in the Chushka — Taman Bay direction and the other was located at the South-West of the Kerch Strait. High concentration of mineral and organic forms of nitrogen was identified there. Concentrations were 1.5–2 times higher than in the center of the shipwreck. Also, high concentration of organic matters and its biochemical labile part in the bottom sediments were discovered to evidence the prevailing of recovery processes. The differences of

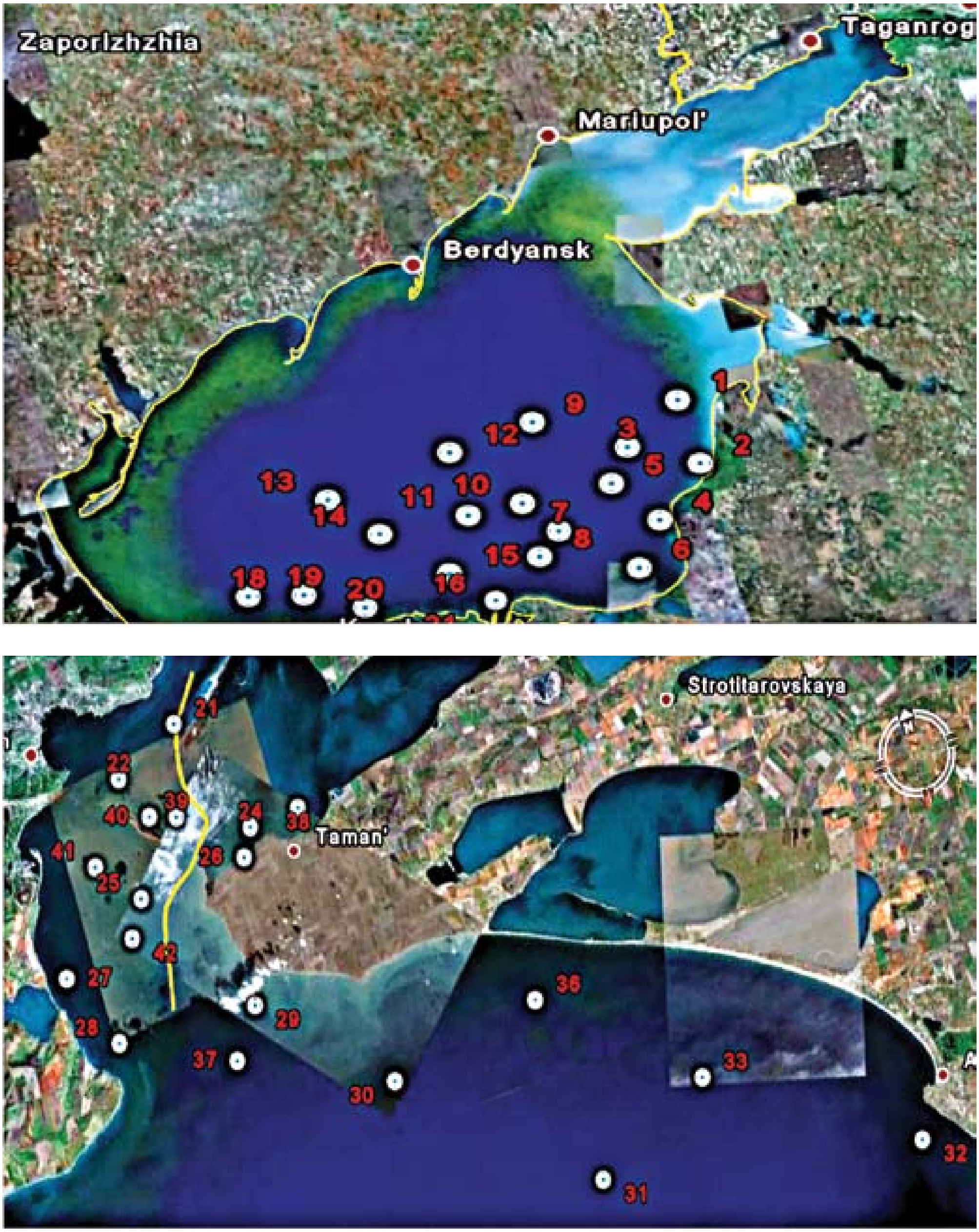

Fig. 5.2.3a. Water and bottom sediments sampling stations in the Azov and Black Seas in the period 30 November–7 December 2007.

values of hydrochemical parameters of water quality and sediments in the selected areas indicate erosion of the oil spot and the flow of contaminated water associated with the transformation of water and sediment towards the Azov Sea. Similar data processing for the Azov Sea allowed identifying the area of residual effect of the shipwreck with the spread of biological pollutions radially from the Kerch Strait (Fig. 5.2.3g).

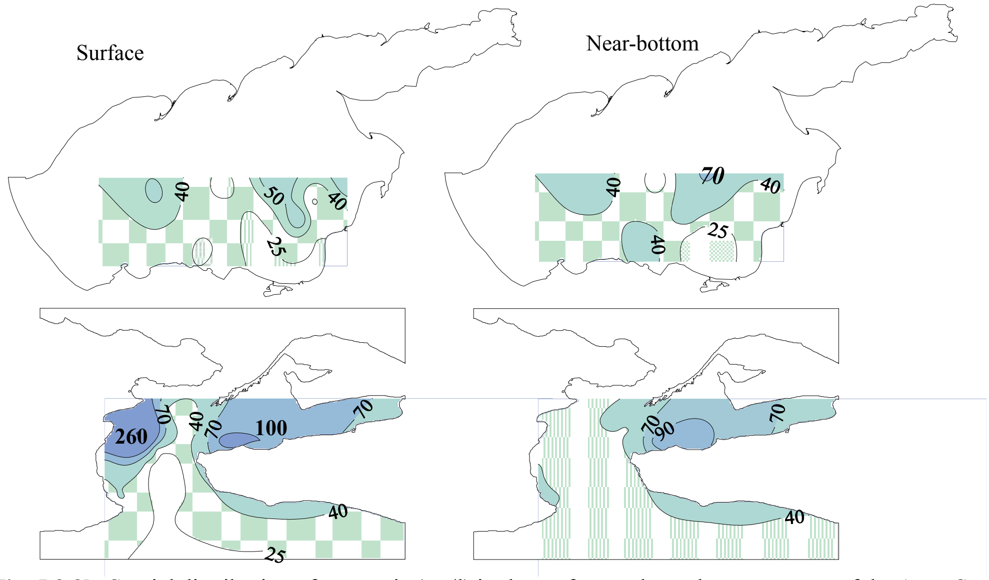

Fig. 5.2.3b. Spatial distribution of ammonia (μg/l) in the surface and near bottom waters of the Azov Sea (upper row) and the Kerch Strait (lower row) in the period of 30.11–07.12.2007.

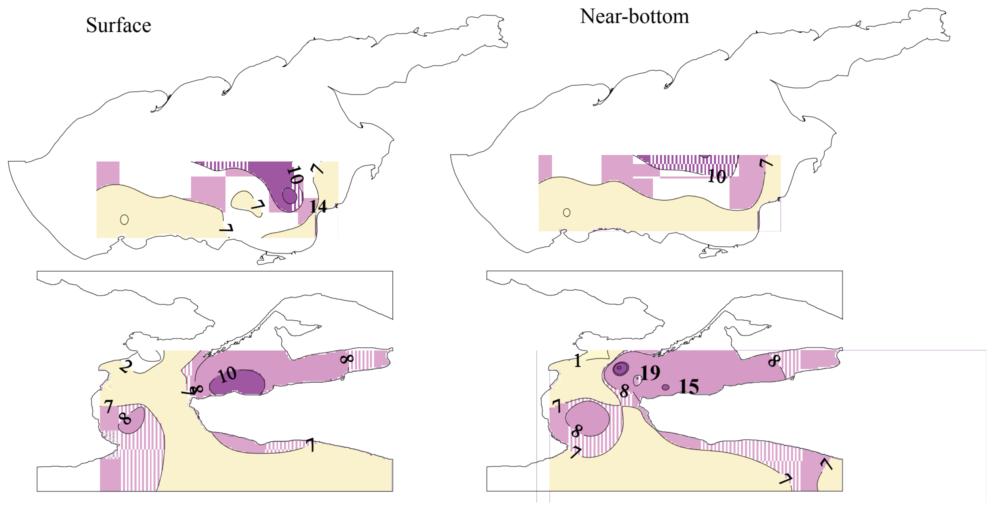

Fig. 5.2.3c. Spatial distribution of nitrites (μg/l) in the surface and near bottom waters of the Azov Sea (upper row) and the Kerch Strait (lower row) in the period of 30.11–07.12.2007.

Table 5.2.3c. Chemical parameters of water and bottom sediments in the patches of residual influence of the Kerch oil spill in the period of 30 November–7 December 2007.

Area	Water, µg/l					Bottom sediments		
	Ammo-nia	Nitrites	Nitrates	Phos-phates	Norg	Corg, %	BOD_1 mgO_2/kg day	Eh, mB
Patch I	55	9	19	17	290	1.23	30	–51
Patch II	42	7	24	28	430	1.0	38	69
Center of accident	31	3	10	21	190	0.19	12	355
Area III (background)	33	6.5	9.7	18	240	0.6	26	48
Azov Sea	48	8.6	44	15	570	3.5	45	+11

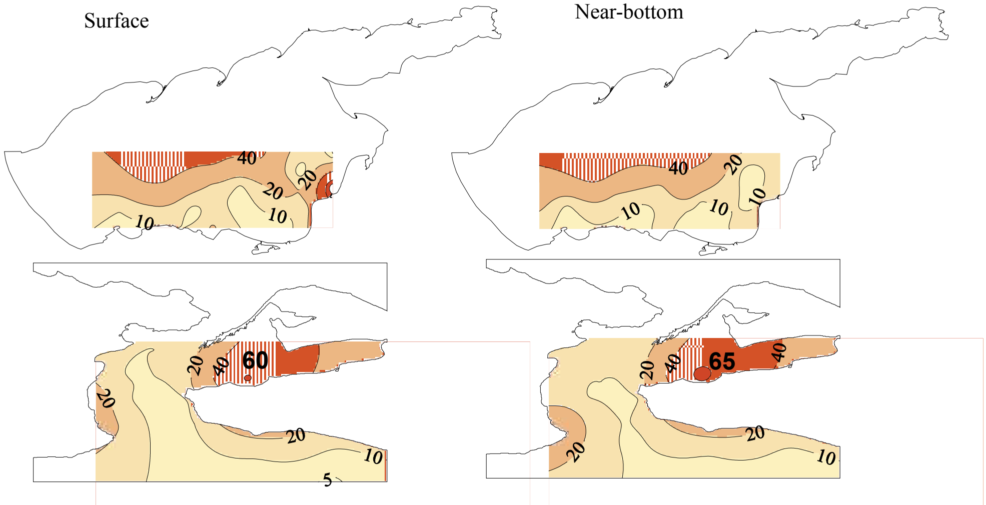

Fig. 5.2.3d. Spatial distribution of nitrates (μg/l) in the surface and near bottom waters of the Azov Sea (upper row) and the Kerch Strait (lower row) in the period of 30.11–07.12.2007.

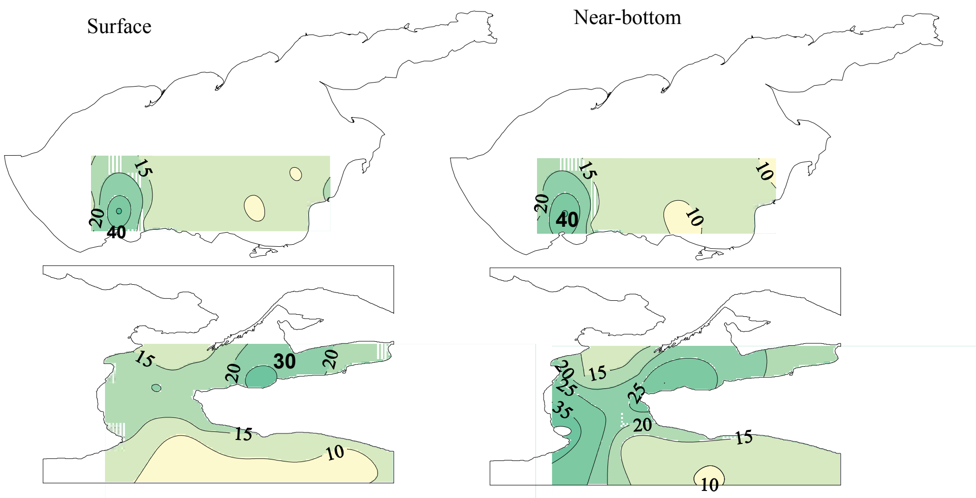

Fig. 5.2.3e. Spatial distribution of phosphates (μg/l) in the surface and near bottom waters of the Azov Sea (upper row) and the Kerch Strait (lower row) in the period of 30.11–07.12.2007.

5.2.4. SSC RAS (Russia): November–December 2007

In the Kerch Strait, the Southern Scientific Centre of the Russian Academy of Sciences (SSC RAS) carried out 4 complex expeditions in November and December 2007 after the Kerch accident with participation of 18 experts specializing in various fields. The investigations included: pollution (petroleum hydrocarbons and trace metals) of the area affected by the accident; hydrological and hydrochemical characteristics of water; state of plankton and benthos communities (including plants and algae); ichthyofauna; ornithofauna on the Taman Peninsula e. g. species composition, distribution, abundance of birds and number of dead birds (Matishov G. G. *et al.,* 2008).

During the first days after the Kerch accident, the field trips were carried out by two groups — at sea and on the coast. The observations and sampling on coast covered the coastal zone of the Taman Bay, Chushka and Tuzla Spits, and the Russian Black Sea coast till the village of Volna (Fig. 5.2.4a). The concentration of petroleum hydrocarbons in the Kerch Strait waters varied in the range of 0.03–0.94 mg/l (18.8 MAC) and in certain areas their content was elevated in the near bottom layer most probably due to the sedimentation of the spilled heavy fuel oil. Less polluted were the inner parts of the Taman and Dinsky Bays and the area near the village of Taman.

From 11 to 15 December 2007, using the *Master 450* boat, 36 CTD profiling stations were covered in the Kerch Strait by SSC RAS. In parallel, meteo-observations, measurements of water transparency (Secci disc), pollution and inorganic forms of nutrients were carried out. Bottom sediments were sampled at 5 stations for pollution and at 30 for investigations of benthos. Compared to mid November, the concentration of TPHs in the water decreased down to the typical for the Strait level of 0.03–0.05 mg/l (Matishov G. G. *et al.,* 2008). However, the part of the spilled heavy fuel oil, which gravitationally sank, got covered with sand and mud on the bottom. Possible re-suspension of this oil under stormy conditions was expected to cause secondary pollution of water and coast in the Kerch Strait.

5.2.5. UkrSCES (Ukraine): July and December 2009

5.2.5.1. *July 2009 Kerch Strait (the 30th Vladymyr Parshin RV)*

In line with the Ukrainian Integrated Ecological Monitoring Program, the Vladimir Parshin scientific research vessel undertook an expedition to the Azov and the Black Seas from 30 June to 10 July 2009 to study the current state of these marine environments. The expedition was divided into two parts. During the first one, the situation was observed at 9 stations in the North-Western part of the Black Sea shelf. During the second part 14 stations were sampled in the Kerch Strait.

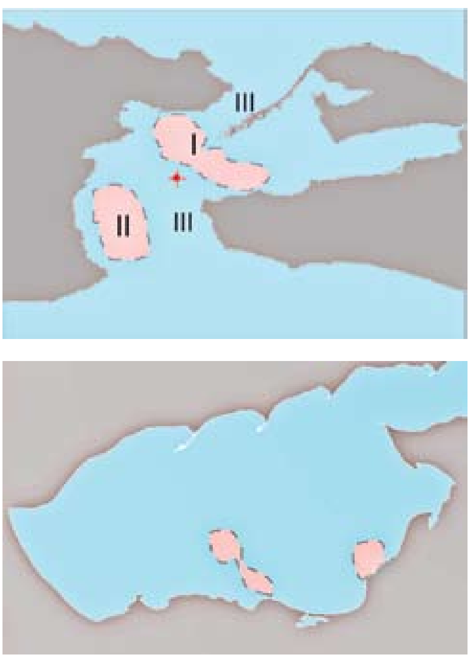

Fig. 5.2.3g. The patches of residual influence of the Kerch oil spill in the Kerch Strait and Azov Sea in the period of 30 November — 7 December 2007.

The objective of the studies was to determine the effect, if any, of the oil spill in November 2007 (Fig. 5.2.5.1a).

At each station, water samples from surface and nearbottom layers were collected. For standard hydrophysical measurements CTD-profiling system were used. Hydrochemistry covered dissolved oxygen concentration and nutrients. Total petroleum hydrocarbons (infra-red spectrophotometer) and aromatic hydrocarbons (spectrofluorometric) concentrations in marine waters are discussed in Chapter 6. In bottom sediments the contents of organic carbon, phenols, total petroleum hydrocarbons (TPHs), PAHs, chlorinated pesticides and trace metals were measured (Chapters 6, 7).

In the Kerch Strait all stations were in shallow waters, mainly at 5–10 m depth and the deepest one sat at 18 m only. Among hydrological parameters, salinity mainly indicated rather uniform water masses present in the Strait on 8 July 2009. Consequently, in these shallow mixed waters some parameters, such as pH showed rather narrow range of variation. In general, the oxygen concentration was high — above 100 % in the whole water column with a single exception in the Northern part of the studied area having at surface a 77.4 % of oxygen saturation only. The averages and ranges of variability of standard hydrochemical parameters sampled in the North-Western part of the Black Sea and in the Kerch Strait in July 2008 have a comparable level of variations (Tab. 5.2.5.1a).

Table 5.2.5.1a. Averages and ranges of variability of standard hydrochemical parameters measured in the North-Western part of the Black Sea and in the Kerch Strait on 08.07.2009, the 30th cruise of the *Vladymyr Parshin* RV.

Parameter	N-W part of the Black Sea				Kerch Strait			
	Surface		Bottom		Surface		Bottom	
	Average	Range	Average	Range	Average	Range	Average	Range
$N\text{-}NH_4$ µg/l	4.7	0–28	2.1	0–7.0	5.7	2.8–9.8	5.3	<0.7–1.4
$N\text{-}NO_2$ µg/l	0.9	0.5–1.8	1.4		1.2	0.7–2.1	2.2	0.7–4.1
$N\text{-}NO_3$ µg/l	4.6	2.9–9.2	5.7		1.5	0.1–3.5	0.6	0–2.9
N_{org} µg/l	220		190		270		230	
N_{total} µg/l	230	140–320	200		299	179–456	239	133–397
$P\text{-}PO_4$ µg/l	11.2	1.9–27.6	17.8	5.2–53.3	8.2	2.8–16.5	11.8	1.6–52.7
P_{total} µg/l	35.3	8–80.0	43.7		27.5	10.2–57.5	35.8	15.1–83.5
pH	8.34	8.28–8.44		8.17–8.24	8.29	8.25–8.31	8.30	8.26–8.36
BOD_5					2.86	1.02–7.12	1.71	0.77–2.57

The average concentration of easily decomposed organic substances in the Strait surface waters, measured by the BOD_5 was 2.89 mg/l which was a rather moderate level. The range of variations was very high allowing distinguishing in between very clean and highly polluted waters. The highest value of BOD_5 was recorded southward from the Tuzla Island. In near bottom layer the organic matter was in low concentrations (on the average of 1.71 mg/l, with variations in the range of 0.77–2.57 mg/l).

Organic nitrogen presented 96 % of the total N in the N-W part of the Black Sea and 90 % in the Kerch Strait. In bottom layers the distribution on N species was similar — 95 % in the North-Western part and 96 % in the Kerch Strait for the organic nitrogen in the amount of total N. Similar to the nitrogen, the organic forms of phosphorus were prevailing — 72 % and 78 % in surface waters of the N-W part and Kerch Strait correspondingly. In bottom layers these shares were — 56 % and 55 %. $P\text{-}PO_4$ maximum was recorded in the deepest waters sampled in the Kerch Strait at the Black Sea entrance to the Strait.

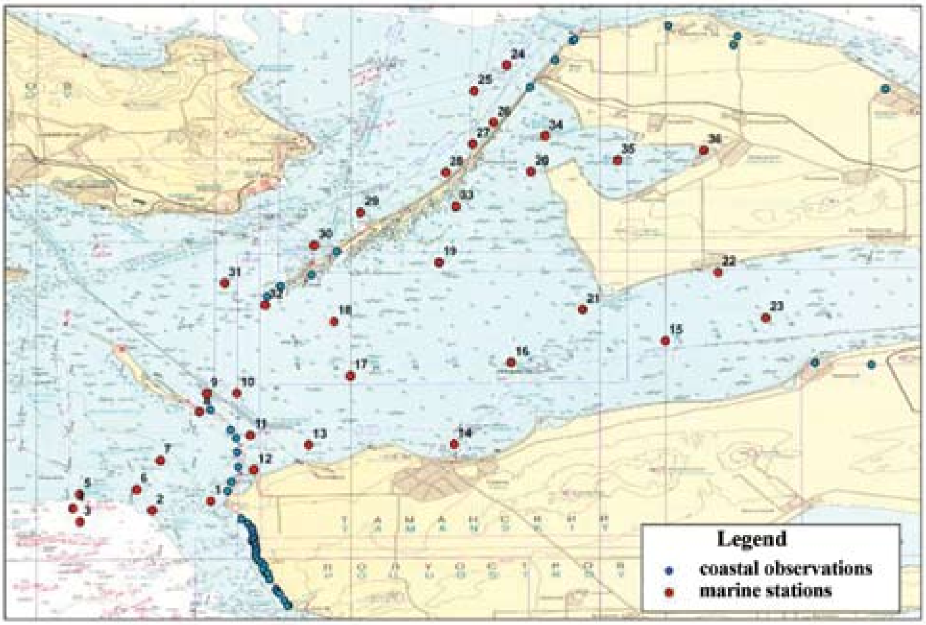

Fig. 5.2.4a. Sea and coastal sampling stations of SSC RAS expedition in November–December 2007.

The measurement undertaken during the summer season did not discover differences between sulphates concentrations in the Kerch Strait and the rest water areas, for example, in the North-Western part of the Black Sea shelf. Concentration of sulphates was of 1.2 g/l to 1.4 g/l. The expected increase in the concentrations of sulphates in the bottom layer of the Kerch Strait due to the sunken ships with sulphur was not discovered.

Concentration of suspended solids (SS) ranged from 1 mg/l to 250 mg/l in the Kerch Strait waters. Maximum concentration of suspended solids was observed in the Southern part of the Kerch Strait and close to the Tuzla Island. The concentration in the bottom layer was normally higher than in the upper ones. The high SS content usually negatively impacted on the bottom fish species and survival of larvae of valuable species, depressing growth of plankton.

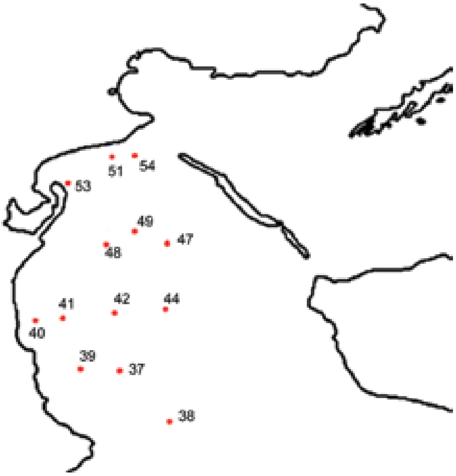

Fig. 5.2.5.1a. Sampling stations in the Kerch Strait during the 30th cruise of the *Vladymyr Parshin* RV on 8 July, 2009.

5.2.5.2. *December 2009 Kerch Strait (the 31^th^ Vladymyr Parshin RV)*

The UkrSCES (Odessa) onboard of the *Vladymyr Parshin* RV (31st cruise) carried out complex investigations on the marine environment in the Azov and Black Seas including North-Western part of the Black Sea in the period of 4–15 December 2009 (Fig. 5.2.5.2a, Fig. 5.2.5.2b).

A wide spectrum of hydrological, hydrochemical, including pollution, and biological parameters were measured. Standard hydrophysical measurements by CTD (including permanent registration of temperature and salinity of surface waters), Secci disk depth, direction and velocity of currents by ADCP were conducted. Hydrochemistry covered nutrients concentration, BOD_5 and organic carbon in the water. Pollutants studied were trace metals, detergents, aliphatic and aromatic hydrocarbons and elemental sulphur. In the bottom sediments the content of organic carbon, phenols, aliphatic, aromatic and polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides from DDT and HCH groups, sulphur and trace metals (Fe, Cd, Co, Hg, Cu, Pb, Cr, Zn, Ni, As, Al) were measured. Pesticides and PAHs in biota (bottom invertebrates) were also investigated. An extended biological programme covered determination of pigments concentration, abundance and biomass of phytoplankton, zooplankton, meiobenthos, phytobenthos, macrozoobenthos and some microbiological parameters. Radiological and geological studies were carried out in parallel. The total number of sampling stations was 85, at which 83 water and 32 bottom sediments samples were collected.

As a rule, concentrations of nutrient substances, oxygen and pH are stabilized due to attenuation of the biochemical processes during the winter period and the range of changes becomes narrower. However, high values of standard deviations indicate considerable variability of concentrations of N_{total} and NH_4 during the 2009 winter period (Table 5.2.5.2a).

The picture of spatial distribution of ammonia nitrogen in the surface and bottom layers in the Kerch Strait indicates a flow of ammonia present in the Black Sea waters as well as the polluted waters presence in areas close to urbanized territories of the central part of the Strait (Fig. 5.2.5.2c).

Table 5.2.5.2a. Statistics of hydrochemical parameters in the Kerch Strait on December 8–11, 2009.

Parameters	N observations	Average	Median	Minimum	Maximum	Standard deviation
Surface layer						
pH	41	8.29	8.28	8.13	8.50	0.10
Oxygen, mg/l	41	9.99	10.33	8.82	11.01	0.64
Oxygen, %	41	97,7	97.7	95.7	101.4	1.29
BOD_5, mg/l	15	1.69	1.84	0.71	2.46	0.51
$N\text{-}NO_2$, µg/l	26	2.01	2.0	0.1	4.7	1.33
$N\text{-}NO_3$, µg/l	26	5.31	5.0	1.0	14.1	3.48
$N\text{-}NH_4$, µg/l	26	7.98	6.8	0.7	31.2	7.38
N_{total}, µg/l	27	543.0	520	137	1071	278.0
$P\text{-}PO_4$, µg/l	41	14.60	13.0	3.90	31.0	8.17
P_{total}, µg/l	27	39.5	38.0	14.0	56.0	10.9
SO_4^{4-}, µg/l	27	866.2	816	624	1296	203.5
Porganic, µg/l	27	25.1	27.4	3.0	50.6	12.91
Norganic, µg/l	27	526.8	507	107	1054	279.8

Corganic, mg/l	27	5.47	4.48	1.88	20.9	3.74
Suspended Solids, mg/l	27	11.63	7.18	1.32	31.80	8.84
Near-bottom layer						
pH	26	8.26	8.27	8.14	8.43	0.07
Oxygen, mg/l	26	10.08	10.36	9.08	10.62	0.55
$BOD_{5,}$ mg/l	14	1.5	1.5	0.4	2.8	0.73
Oxygen, %	26	96.90	96.9	95.5	99.0	0.98
$N\text{-}NO_{2,}$ µg/l	27	1.95	1.7	0.1	6.9	1.58
$N\text{-}NO_{3,}$ µg/l	27	5.91	2.8	0.1	35.2	7.71
$N\text{-}NH_4$, µg/l	27	7.49	6.7	0.7	29.6	6.63
N_{total}, µg/l	25	567.7	660	70	996	296.1
$P\text{-}PO_{4,}$µg/l	26	15.97	15	3.9	36.1	10.08
$P_{total,}$µg/l	25	47.16	42	21.2	108	19.26
SO_4^{2-},µg/l	23	872.3	864	552	1464	210.1
Porganic,µg/l	25	31.5	31	0.0	85	21.21
Norganic, µg/l	25	551.7	624	62	989	293.6
Corganic, mg/l	24	8.08	5.61	2.21	37.10	8.38
Suspended Solids, mg/l	25	13.77	13.30	2.16	52.70	11.38

Minor standard deviations and close values of average and median of $N\text{-}NO_2$ concentrations point to its little variations in surface and bottom layers (Table 5.2.5.2a). In general, spatial distribution of nitrites (Fig. 5.2.5.2d) was similar to ammonia. Concentrations of nitrates were not high, accompanied by insignificant variability. Prevalence of ammonium nitrogen in its oxidized forms should be noted. Most probably, during the observation period, the process of mineralization of organic matter was at the initial stage of its development.

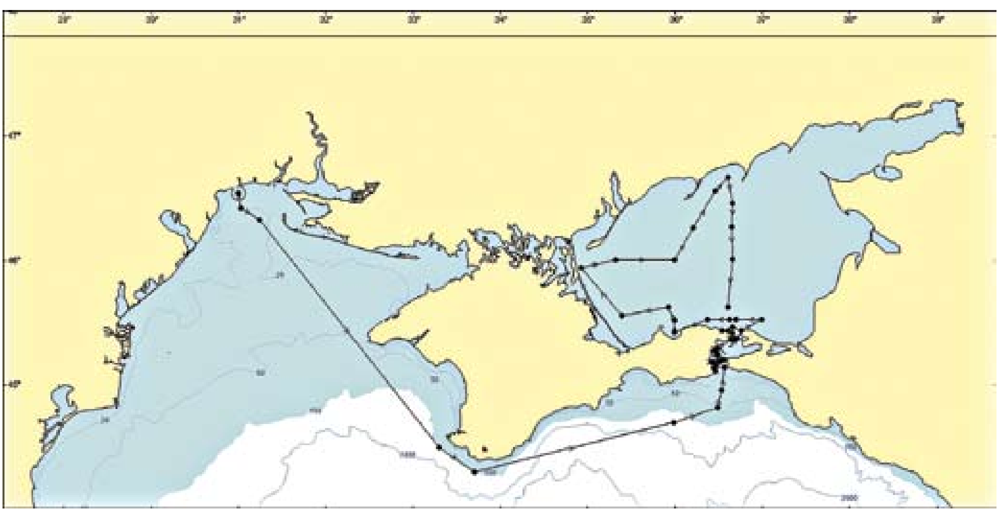

Fig. 5.2.5.2a. Map of sampling stations in the Azov and Black Seas during the 31st cruise of the *Vladymyr Parshin* RV in the period of 4–15 December 2009.

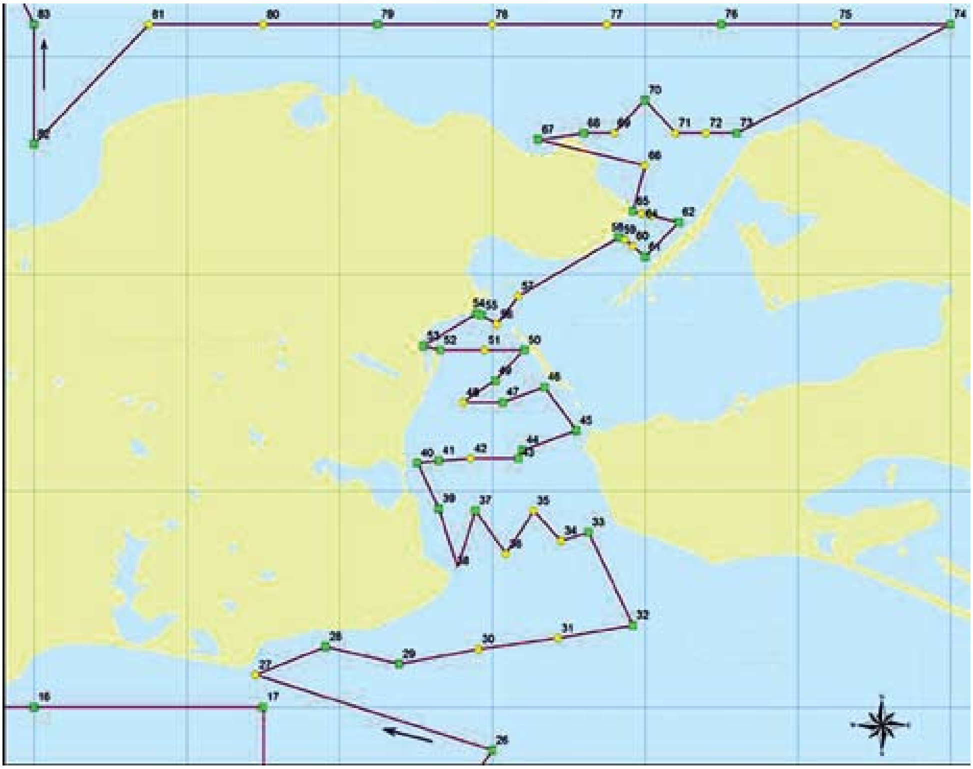

Fig. 5.2.5.2b. Stations in the Kerch Strait sampled during the 31st cruise of the *Vladymyr Parshin* RV in the period of 4–15 December 2009.

A relatively high level of total nitrogen was discovered. Organic form of nitrogen prevailed over the mineral during the winter period similarly to the summer period. Judging from the standard deviation, spatial variability of concentrations of organic nitrogen was high (Table 5.2.5.2a). Organic form of phosphorus prevailed over the mineral one. Zones of high concentrations of P_{total} and $P\text{-}PO_4$ were located closely to the costal pollution sources, similarly to the nitrogen zones observed (Fig. 5.2.5.2e).

Dissolved oxygen in the surface waters of the Kerch Strait varied broadly. The spatial distribution of oxygen in the waters of the Kerch Strait demonstrates that higher concentrations of oxygen in 2009 winter were discovered in the Northern part of the Strait due to cold water flow from the Azov Sea. In the deep waters spatial distribution of dissolved oxygen concentration remained near identical to surface indicating the absence of vertical gradients in shallow waters (Fig. 5.2.5.2f).

Maximum rates of BOD_5 were discovered in the Northern part of the Strait. However, absolute values were significantly lower than in summer. The maps of spatial distribution show that zone of maximum easy oxidized organic matter in the surface and bottom layers of water were similar to spatial distribution of nutrients and they were related to the land based sources of pollution (Fig. 5.2.5.2g).

Unlike during summer, in December 2009 high concentration of sulphates was recorded in the near-bottom waters in the Kerch Strait. In upper layer their content was also rather high and varied from 624 to 1296 mg/l. However, these values were not related to the Kerch accident.

Studies have shown that the content of nutrients and easily oxidized organic matter in waters of Kerch Strait is slightly higher compared with other areas of the Black and Azov Seas. The high background concentrations were well associated with external sources of various forms of nutrients and organic matter in the marine environment, and most probably due to intensive human pressure. It is well known that intense flow of mineral and organic forms of nutrients is accompanied by increased photosynthetic processes and the creation of a larger primary production which results in eutrophication. The signs of this process are the relatively high levels of BOD_5 and consequent reduction of oxygen saturation in the near-bottom waters. Another indicator of an active redox processes is concentration of ammonium and nitrite nitrogen. Their relatively high concentration signals the inflow of large quantities of organic substances.

5.2.6. MHI (Ukriane): December 2009 Kerch Strait near Tuzla Island

Short one-day screening of hydrochemical conditions in the surface waters of the Kerch Strait was carried out by MHI and MB UHMI (Sevastopol, Crimea) at 18 stations nearby the Tuzla Island on 4 December 2009. Standard parameters (salinity, dissolved oxygen, pH and silicates) distribution was well related to a dominating Azov waters outflow to the Black Sea. The water parameters values were close to those in the Black Sea only at the South-Eastern side of the Tuzla Island.

Oxygen concentrations varied in the range of 9.3–11.1 mg/l and saturation was rather uniform — of 98–101 % in all studied area. Similar to the latter, the pH distribution was rather even within the range of 8.3–8.37, with only two lower values of 6.83 и 6.98 pH (to the North of the Tuzla Island) which might be outliers related to technical problems with equipment.

Among nutrients the concentration of phosphates was lower than the Detection Limit of 10 µg/l except for one station northward of Tuzla where 12 µg/l of $P–PO_4$ were measured. The content of total phosphorus reached the level of 24 µg/l and higher concentrations were mainly located in the Northern part of the Strait, obviously under the influence of the Azov Sea waters.

The nitrites concentration was lower than the Detection Limit of 5 µg/l. The same situation occurred for nitrates and ammonia (DL=10 µg/l) with exception of two stations near the Northern side of Tuzla having the mentioned forms of nitrogen in the range of 15–22 µg/l. The total nitrogen concentration reached 426 µg/l and the ratio of N_{total}/P_{total} stands at 18 in December 2009, being close to Redfield ratio, whereas it was 40 in February 2008.

The detergents and phenol concentrations were lower than DL at all stations, 25 and 3 µg/l correspondingly.

5.2.7. YugNIRO (Ukraine): November 2007–March 2009

The Institute conducted 7 field trips in the Central and South parts of the Kerch Strait in the period of November 2007-March 2009, as is described in Annex 2. The considerable increase in monitoring effort after the Kerch accident was evidenced by 8 field trips in 2002–2007 versus 7 cruises in less than 1.5 year after the catastrophe. Among standard hydrochemical investigations, salinity, pH, dissolved oxygen, BOD_5, sulphur and different forms of nutrients were measured in surface and near bottom layers. The sampling stations were placed mainly in the transshipment anchor place located South to the Tuzla Island (12 stations) and in the Kerch Bight (6 stations).

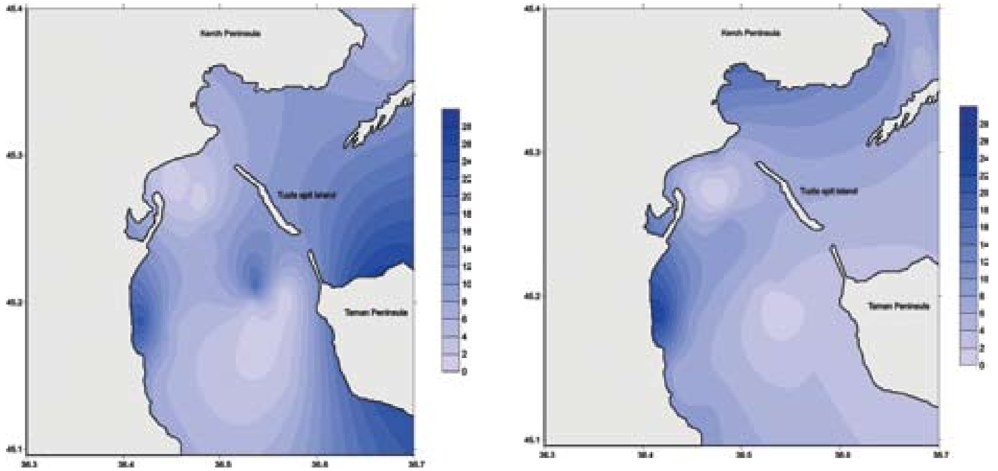

Fig. 5.2.5.2c. Ammonia distribution (µg/l) in the upper (left) and near-bottom (right) layers in the Kerch Strait on December 8–11, 2009 (the 31th cruise of the *V. Parshin* RV).

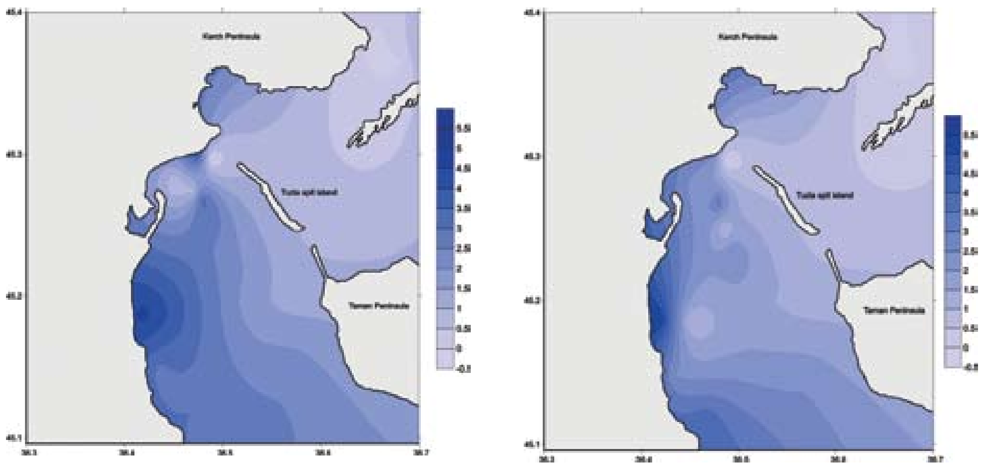

Fig. 5.2.5.2d. Distribution of nitrites (µg/l) in the upper (left) and near-bottom (right) layers in the Kerch Strait on December 8–11, 2009 (the 31[th] cruise of the *V. Parshin* RV).

After the Kerch accident, TPHs and sulphur concentrations were measured annually at six stations in the central part of the Strait (Sebah L. K. *et al.,* 2008, Sebah L. K. *et al.,* 2010, Zhugailo S. S. *et al.,* 2011).

Traditionally, salinity was lower in the upper layer and interannually there was no trend in its variability (Table 5.2.7a). In the whole water column pH varied insignificantly, with general increase from spring to autumn related to active photosynthesis.

The dissolved oxygen concentration varied in a very wide range. In surface water the oxygen regime was without deviation from the norm. In the near-bottom water oxygen was lower than at surface, with minimal value of 3.80 mgO_2/l observed in November 2007. However, water temperature was the main influencing factor on the oxygen variability.

After the Kerch accident, the BOD_5 level was below 3.0 mgO_2/l and the values observed did not show abnormality (usually, minimal values of BOD_5 are recorded in winter). Maximal values were observed in autumn 2009 — 4.22 mgO_2/l, unrelated to the accident.

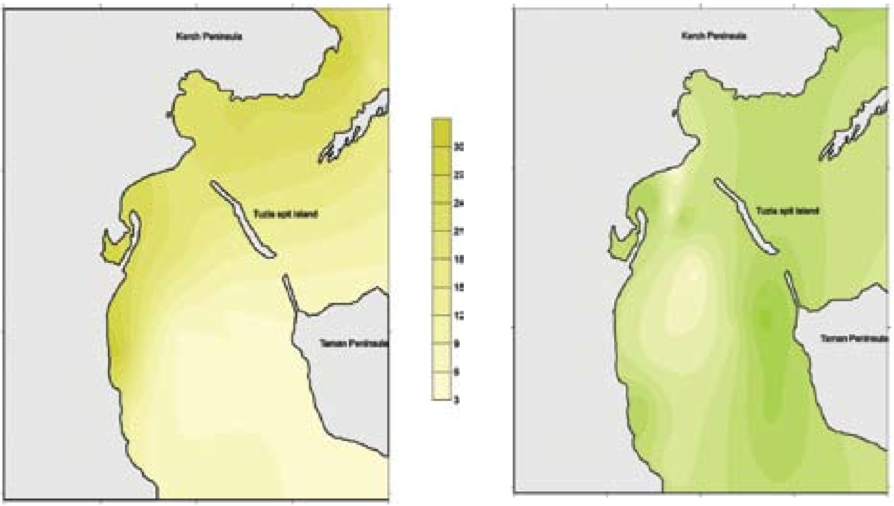

Fig. 5.2.5.2e. Concentration (µg/l) of phosphates (left) and total phosphorus (right) in the Kerch Strait surface waters on December 8–11, 2009 (the 31[th] cruise of the *V. Parshin* RV).

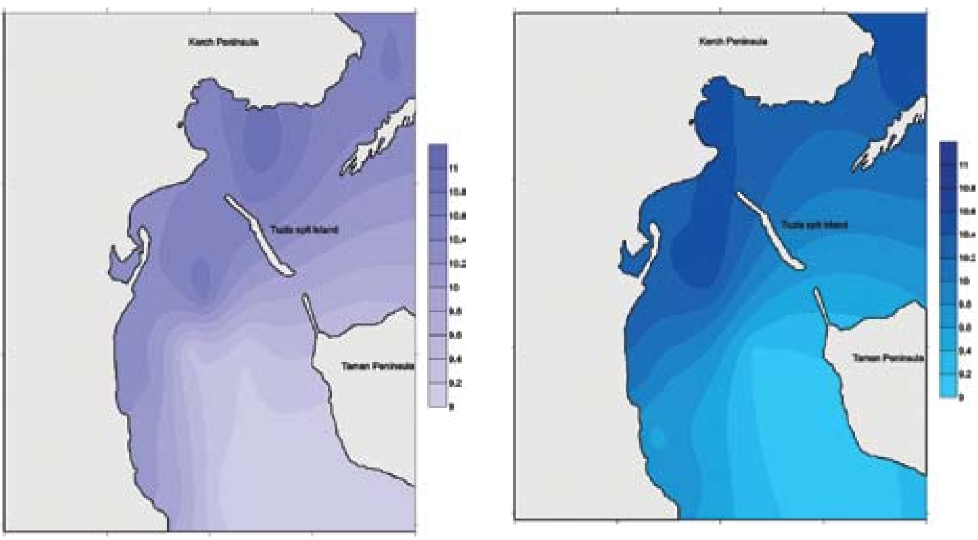

Fig. 5.2.5.2f. Concentration (mg/l) of dissolved oxygen in the upper (left) and near-bottom (right) layers in the Kerch Strait on December 8–11, 2009 (the 31[th] cruise of the *V. Parshin* RV).

Table 5.2.7a. Concentration of hydrochemical parameters in the Kerch Strait in 2007–2009.

Date	Salinity, ‰			pH			Oxygen, mg/l			BOD_5, mgO_2/l		
	Aver.	Min.	Max.	Aver.	Min.	Max.	Aver.	Min.	Max.	Aver.	Min.	Max.
Surface layer												
09.2007	–	17.60	17.96	8.17	8.05	8.21	6.89	6.33	7.33	1.27	0.30	2.29
10.2007	–	17.50	17.82	8.35	8.10	8.49	8.42	8.21	9.11	1.14	0.64	2.40
02.2008	16.20	11.69	17.84	8.58	8.32	8.70	11.14	9.37	13.23	1.18	0.60	2.59
04.2008	16.64	16.37	17.15	8.28	8.02	8.35	8.38	8.10	8.69	0.98	0.36	1.57
09.2008	16.38	14.76	17.78	8.40	8.15	8.45	7.88	6.84	8.71	0.93	0.04	1.59
11.2008	17.82	17.65	17.95	8.47	8.20	8.56	9.36	8.44	10.18	0.64	0.04	1.20

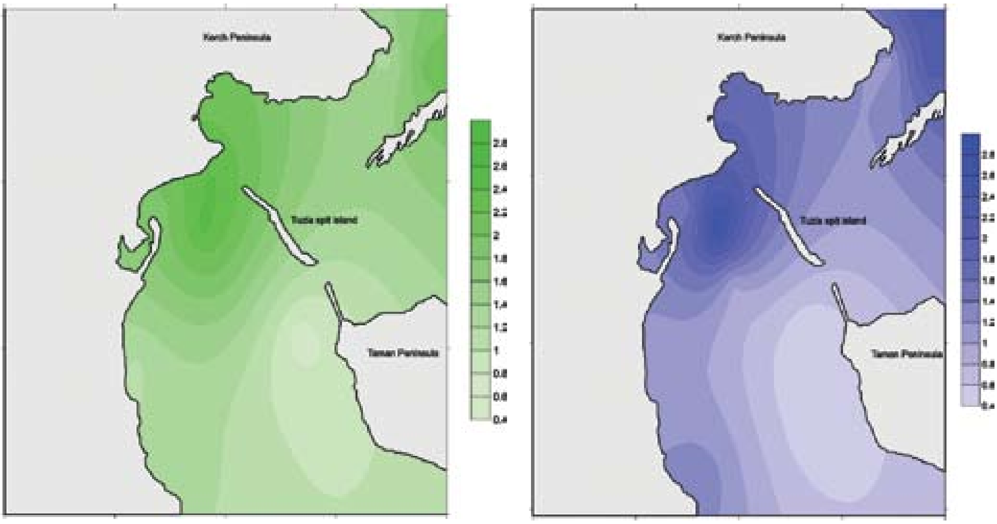

Fig. 5.2.5.2g. Concentration (mg O_2/l) of organic matter measured by BOD_5 in the upper (left) and near-bottom (right) layers in the Kerch Strait on December 8–11, 2009 (the 31[th] cruise of the *V. Parshin* RV).

03.2009	11.13	10.72	13.10	8.34	8.00	8.42	11.42	10.21	12.37	1.04	0.01	1.82
06.2009	16.11	16.34	17.21	8.35	8.32	8.37	8.38	7.82-	8.85	1.44	0.83	2.22
09.2009	17.15	17.03	17.15	8.44	8.42	8.47	7.93	6.05	10.10	0.75	0.34	1.30
10.2009	15.26	17.49	17.86	8.52	8.49	8.55	8.92	8.54	9.28	0.85	0.07	1.81
Near-bottom layer												
09.2007	–	17.75	18.02	8.17	8.07	8.21	6.27	3.80	7.19	2.11	1.13	3.83
10.2007	–	17.62	17.80	8.35	8.07	8.42	8.41	8.01	9.18	1.08	0.94	1.92
02.2008	16.99	15.40	17.84	8.54	8.05	8.65	10.58	9.40	11.49	0.85	0.51	1.60
04.2008	16.83	16.57	17.13	8.28	8.10	8.35	8.09	7.63	8.35	1.35	0.59	1.77
09.2008	17.33	15.48	17.84	8.4	8.30	8.45	7.58	4.82	8.28	1.26	0.70	2.02
11.2008	17.82	17.62	17.98	8.49	8.27	8.56	9.09	5.65	9.94	0.97	0.06	2.30
03.2009	16.91	16.46	17.35	8.35	8.10	8.42	9.77	8.04	10.67	0.49	0.10	1.56
06.2009	16.86	17.01	17.98	8.30	8.15	8.37	9.00	8.34	9.49	2.43	1.14	3.53
09.2009	17.10	13.74	16.60	8.45	8.42	8.45	7.81	7.22	8.14	1.22	0.31	4.22
10.2009	17.73	16.34	17.21	8.49	8.43	8.53	8.46	7.56	9.13	0.96	0.07	2.15

In 1998–2007 the increasing content of mineral nitrogen in the waters of the Strait followed on the intensification of re-loading of fertilizers in the transshipment area south to the Tuzla Island (Table 5.2.7b). Later this practice was terminated but concentration of some nutrients remained rather high. Maximal levels were recorded in the Northern-Western part during all period of investigations. The latter could be dependent on the water dynamics changes after the dam construction at the Tuzla Spit (Goriachkin Yu. N. *et al.,* 2007, Ovsienko S. N. *et al.,* 2008).

The average concentration of ammonia and nitrites in the near-bottom layer was higher than at surface. Ammonia maximum was usually recorded in spring which is not typical for marine environments. Nitrates level was increased during all seasons.

Sulphates concentration after the Kerch accident did not change atypically. In general, averages were in the range of the long-term interannual variability and varied from 1.22 g/l to 1.43 g/l.

Table 5.2.7b. Concentration of mineral nitrogen in the Kerch Strait in 2007–2009.

Date	$N\text{-}NH_4$, µg/l			$N\text{-}NO_2$, µg/l			$N\text{-}NO_3$, µg/l		
	Aver.	Min.	Max.	Aver.	Min.	Max.	Aver.	Min.	Max.
Surface layer									
09.2007	11.7	0.0	38.9	3.0	3.0	3.0	114.6	4.5	603.4
10.2007	21.8	1.6	101.1	3.0	3.0	3.0	61.5	24.9	205.7
02.2008	45.1	15.6	101.1	3.6	2.7	6.1	25.5	6.8	81.4
04.2008	10.9	3.9	23.3	2.7	0.9	3.0	49.5	1.1	488.2
09.2008	14.8	7.8	31.1	4.0	3.0	6.1	29.4	18.1	65.5
11.2008	10.1	0.0	85.6	0.0	0.0	0.0	31.9	9.0	146.9
03.2009	38.1	23.3	62.2	3.0	3.0	3.0	14.0	6.8	20.3
06.2009	0.8	0.0	7.8	3.0	3.0	3.0	17.2	9.0	63.3
09.2009	14.0	0.0	23.3	1.8	0.0	3.0	21.0	18.1	38.4
10.2009	29.6	15.6	54.5	4.0	3.0	6.1	20.1	11.3	42.9
Near-bottom layer									
09.2007	18.7	3.9	62.2	3.0	3.0	3.0	25.5	9.04	106.22
10.2007	39.7	7.8	163.4	5.2	0.3	9.1	63.7	27.12	230.52
02.2008	64.6	15.6	140.0	4.3	3.0	9.1	35.5	4.52	135.6
04.2008	25.7	23.3	31.1	3.0	3.0	3.0	24.9	1.13	101.7
09.2008	25.7	15.6	46.7	4.9	3.0	18.2	33.7	15.82	128.82
11.2008	7.8	0.0	85.6	0.0	0.0	0.0	20.8	9.04	74.58
03.2009	59.1	38.9	77.8	4.6	3.0	6.1	11.3	6.78	24.86
06.2009	21.8	0.0	7.8	3.3	3.0	6.1	18.1	9.04	92.66
09.2009	29.6	15.6	62.2	3.6	3.0	6.1	21.0	15.82	33.9
10.2009	6.2	0.0	31.1	3.0	3.0	3.0	25.5	13.56	42.94

5.2.8. Nutrients exchange between the Black and Azov Seas in 2008–2009

Data observed at the cross-section of the ports Crimea — Caucasus in the Ukrainian water area in 2008–2009 were used to calculate nutrients exchange between the Azov and Black Seas (Fig. 1a). Hydrological parameters investigated were: temperature and salinity, flows directions and velocity. In addition, transparency, water color and meteorological parameters (wind directions and velocity, air temperature and humidity, atmospheric pressure, clouds) and waves were measured.

The methodology used to calculate the nutrients flow through the Northern narrowest place of the Kerch Strait was developed as follows. Flows and nutrient concentrations measured at different stations in 1981–1998 were linearly interpolated to the nodes of a grid with a step of 100 m horizontally and 1 m vertically. Then, flow of matters was identified for the total cross section and for the Ukrainian part separately. According to the obtained flow values, flow charts of the scattering were established. Then, based on a result of regression analysis and data collected at the Ukrainian part of the cross section, the equation for calculating the nutrients flow from the Ukrainian part were identified. It should be noted that zero flow cases were not included in the analysis for non-organic forms of nitrogen (nitrites and nitrates). The results of studies showed that flow of each element can be adequately represented in the form of equations of linear regression.

The equations allowed calculating matters flows through the Northern narrowest place of the Kerch Strait for 2008–2009. Due to the lack of data for establishment of regressions, nitrogen flows were calculated for the Ukrainian part of the Strait only.

The analysis of field observation data collected showed that the flow is unidirectional in the narrow parts of the Strait and is characterized by considerable variability in large parts of it. At the direction there are three distinct types of flows: the Azov, Black Sea and the mixed one. First two are fairly stable and provide the greatest water flow, so it makes sense to consider the flow of nutrients according to the predominant flows. It should be mentioned that the Azov and Black Sea flows are fairly easily identified by their different thermohaline structure of water and hydrochemical characteristics.

The predominance of the water flow from the Sea of Azov to the Black Sea is typical for the Strait since this was observed by about 47 % of the total number of observations (Altman E. N., 1975, 1976, Simonov A. I., Altman E. N., 1991). The repeatability of Azov flow was 46 % in 2008–2009 which is close to the mean rate (Fig. 5.2.8a). This transfer occurs when winds are northerly, as well as determined by the dynamics of river flows into the Azov Sea. The Azov Sea flows dominated in June–July 2008 and in April–May 2009. The average discharge from the Azov Sea was 3530 m^3/sec during 2008–2009 with maximum of 7570 m^3/sec.

The Black Sea types of flows are mostly formed by winds of the Southern directions. Its rate was 33 % of the total number of observations in 2008–2009. The frequency of mixed flows of variable directions was 21 %. The Black Sea and mixed flow prevailed in April and May and in August-October 2008. The average discharge of the Black Sea flow was about 3120 m^3/sec and maximum as of 7820 m^3/sec.

The positive flow values of nitrites, total nitrogen, and phosphorus in 2008–2009 are those to the Kerch Strait and to the Black Sea and the negative ones are to the Azov Sea (Fig. 5.2.8a–5.2.8d). Nitrites flow to the Azov Sea through the Northern narrowest place were observed in May (8.07 g/sec), in August (from 0.17 g/sec to 0.37 g/sec), and in September (from 5.07 g/sec to 5.19 g/sec) 2008. Nitrites were moving to the Kerch Strait from the Azov Sea in September (from 2.02 g/sec to 3.86 g/sec), in October (0.59 g/sec), and in June (0.97 g/sec) 2009.

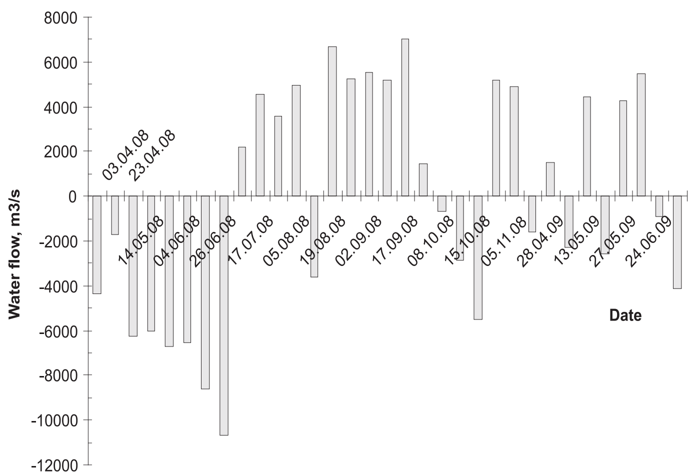

Fig. 5.2.8a. The calculated water exchange (m^3/sec) between the Azov and Black Seas across the Kerch Strait in 2008–2009. Plus is related to the water inflow from the Azov to Black Sea and minus — to the backward outflow.

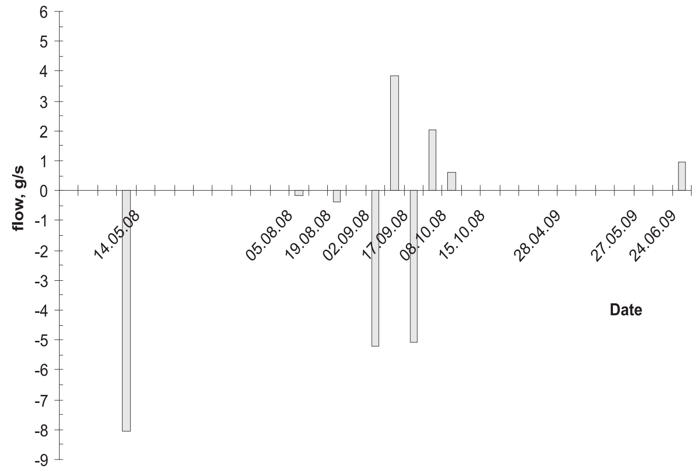

Fig. 5.2.8b. The calculated nitrites exchange (g/sec) between the Azov and Black Seas across the northern narrowest place of the Kerch Strait in 2008–2009.

Flow of ammonia nitrogen from the Azov Sea prevailed during the spring 2008 (from 115 g/sec to 210 g/sec). This inflow of ammonia into the Kerch Strait and further to the Black Sea was calculated for the whole observation period. The outflow varied from 40 g/sec to 154 g/sec during the spring season and from 3 g/sec to 60 g/sec during the summer and autumn seasons.

The total nitrogen flows through the Northern narrowness of the Strait from the Azov Sea was observed more frequently (Fig. 5.2.8c). However, this discharge was much lower and varied from 50 g/sec to 2900 g/sec. The opposite flow brings N_{total} into the Azov Sea at higher intensity of 500 to 4500 g/sec.

Total phosphorus flow dominated throughout the period of observation in 2008–2009 with the Azov Sea waters passing through the Kerch Strait into the Black Sea. Its capacity varied from 15 g/sec to 1500 g/sec. The discharge of phosphorus into the Azov Sea was in order of magnitude lower from 23 g/sec to 140 g/sec (Fig. 5.2.8d).

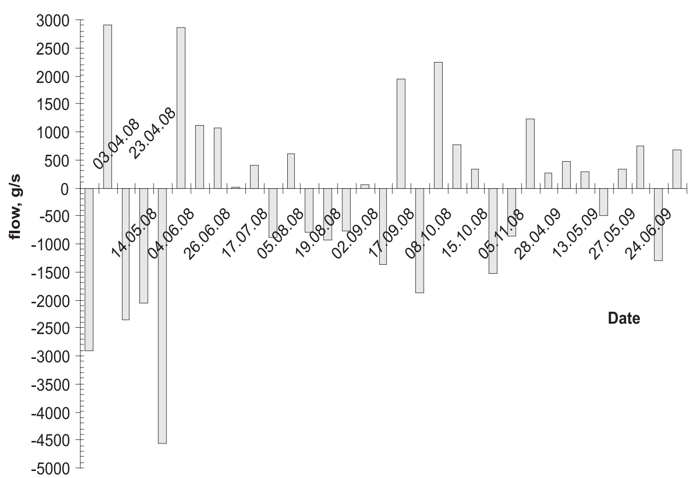

Fig. 5.2.8c. The calculated total nitrogen exchange (g/sec) between the Azov and Black Seas across the northern narrowest place of the Kerch Strait in 2008–2009.

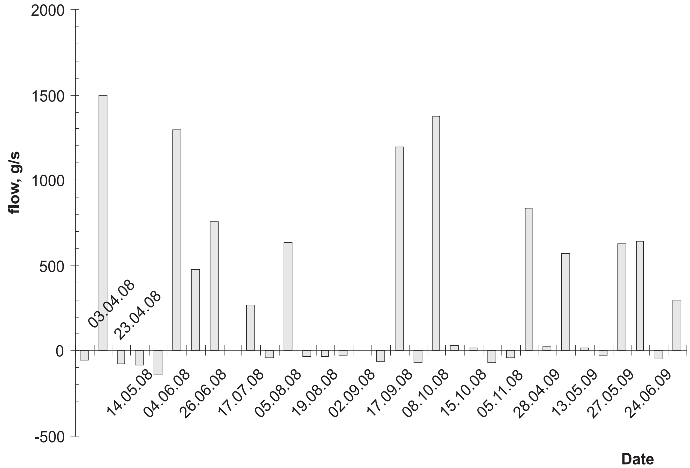

Fig. 5.2.8d. The calculated total phosphorus exchange (g/sec) between the Azov and Black Seas across the northern narrowest place of the Kerch Strait in 2008–2009.

5.2.9. Summary: Standard hydrochemical parameters

There were no long-term visible consequences reflected in the standard hydrochemical parameters of the Kerch Strait waters that could be related to the heavy oil spill accident on 11 November 2007. Rather classical distribution of chemical parameters has been registered soon after the accident, which can be described as follow. In general, the shallow waters of the Strait significantly differ from the adjacent areas of the Azov and Black Seas. Usually, it is expressed by an increased content of nutrients and some pollutants, especially in those areas of the Strait located close to the coasts. The level of nutrients, suspended matter and pollutants in the Kerch Strait is higher than in the North-Eastern part of the Black Sea. The increased baseline concentrations of nutrients are quite stable in these waters and well related to external land-based or ship-borne sources. The calculations of nutrients transportation clearly reflect a main flow from the Azov to the Black Sea for many substances, including total phosphorus, however, total nitrogen indicates opposite tendency. Despite of the high level of nutrients, the waters in the Strait are well saturated with oxygen; no hypoxic or anoxic situations have been ever registered. In some cases low content of oxygen in bottom layers occurs but without consequent mass mortalities of organisms. The complex Index of Water Pollution indicates the «clean» or «moderately polluted» water quality in the period 2003–2008. Despite of the oil spill accident in November 2007, the waters in the Strait have been still qualified as «clean» though IWP slightly increased to 0.52.