

## Chapter 7. Other pollutants in the Kerch Strait

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## 7.1. Observations carried out prior to the Kerch Strait accident

### 7.1.1. UA: YugNIRO. Trace metals present in the bottom sediments in 1995–2000

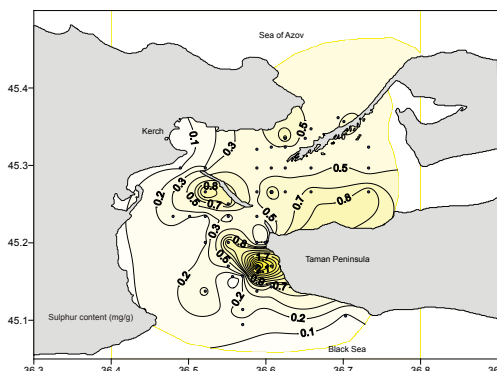
During the period of 1995–2000, average concentrations of manganese, copper, lead, chromium and mercury in the Kerch Strait bottom sediments remained at the background level established for the area (Mytropolsky A. Yu., Bezborod A. A., Ovsyani E. I., 1982). On the contrary, high concentrations of arsenic, cadmium, zinc and iron were registered. Due to the anthropogenic influence, arsenic content had visibly increased in the Kerch Strait in the late 1990s compared to the previously investigated periods and its annual average varied in the range of 20.5–42.5  $\mu\text{g/g}$  of dry weight (background value is 11  $\mu\text{g/g}$ ), (Zhugailo S. S. *et al.*, 2008). However, a generally decreasing trend of the Kerch Bight water column and bottom sediments pollution by trace metals was observed in the period from 1995 to 2000.

## 7.2. The post-disaster observations

### 7.2.1. RU: ChAD. Sulphur content of bottom sediments in July, August, November and December 2008

More than 6500 tons of sulphur was washed out after the vessels accident in November 2007 on the Kerch Strait. Following up on it, Rospirodnadzor carried out in July/August, November and December in 2008 several expeditions at 150 Kerch Strait stations to study the sulphur presence in the bottom sediments upper layer.

Certain similarities were found in the sulphur and TPHs distribution patterns in the bottom sediments (Fig. 7.2.1a).



**Fig. 7.2.1a.** Sulphur concentration (mg/g) of the Kerch Strait bottom sediments in summer 2008.

In 2008, sulphur concentrations were exceeding their typical values at a large bottom area of the Kerch Strait with the maximal values detected in summer (Table 7.2.1a). The maximal sulphur concentration recorded in July-August stood at an extremely high level of 2.87 mg/g (almost 18- fold higher than MAC, as MAC for sulphur was equal to 0.16 mg/g, according to the Russian State Normative 2.1.7.2041–06). The values observed in November-December 2008 were much lower.

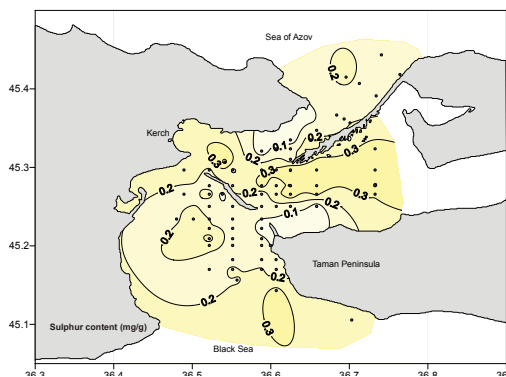
In July-August 2008, sulphur and TPHs were found accumulated in the vicinity of the Taman Peninsula South-Western part, i. e., between the Panagia and Tuzla Capes, and in the Southern direction from the Enikale Cape in the Crimea area.

**Table 7.2.1a.** Statistical parameters of sulphur concentration (mg/g) in the Kerch Strait bottom sediments in 2008.

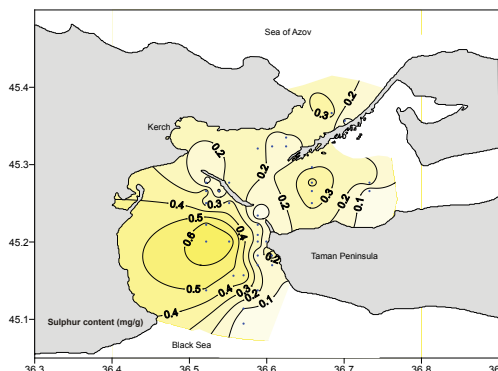
	Number of stations	min	max	Range	Average	Standard deviation	>MAC/%*
<b>Stage 1. July–August</b>							
Sulphur	43	0.08	2.87	2.79	0.5198	0.5271	40/93%
<b>Stage 2. November</b>							
Sulphur	71	0.01	0.43	0.42	0.205	0.0978	45/63%
<b>Stage 3. December</b>							
Sulphur	36	0.02	0.67	0.65	0.267	0.177	25/69%

\*Note: >MAC/% (e. g. 40/93%) stands for the number and percentage of stations where sulphur concentration was exceeding MAC.

The autumn maximal value was almost 7-fold lower than in summer (Fig. 7.2.1b). In November, a high sulphur concentration area covered the Taman Bay and the Kerch Strait area in the proximity of the Kerch Bay, as well as the northwards to the Tuzla Island. Thus, 63% of sediment samples had revealed sulphur concentrations exceeding the normative value.

**Fig. 7.2.1b.** Sulphur concentration (mg/g) of the Kerch Strait bottom sediments in November 2008.

In December, the average and maximal sulphur concentrations registered were slightly increased in comparison with those recorded in November, while their spatial distribution had somehow changed. The high concentration areas with levels >0.6 mg/g i. e., about 4-times higher than 1 MAC, had emerged southwards to the Tuzla Island (Fig. 7.2.1c) and within the Taman Bay (the same as in the previous month). The minimal sulphur concentration was detected at the Kerch Strait exit to the Black Sea.

**Fig. 7.2.1c.** Sulphur concentration (mg/g) of the Kerch Strait bottom sediments in December 2008.

Sulphur content was exceeding MAC at 69% of stations surveyed in December 2008 (Fig. 7.2.1d).

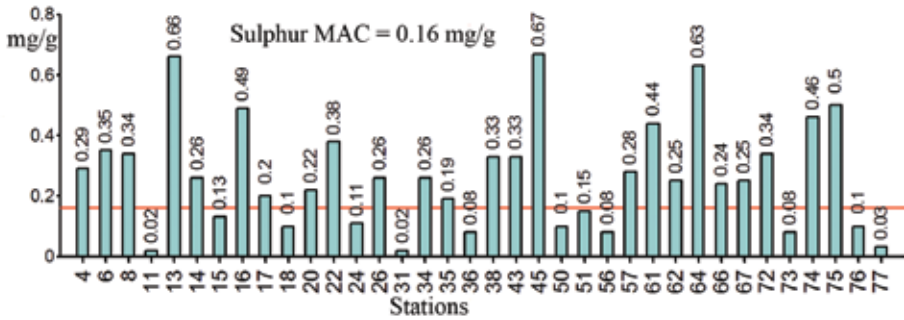


Fig. 7.2.1d. Sulphur concentration (mg/g) of the Kerch Strait bottom sediments in December 2008.

In conclusion, the average July, November and December 2008 sulphur concentrations were exceeding MAC by 3.25, 1.3 and 1.67 times, respectively. Those sulphur concentrations varied in the range of 0.01–2.87 mg/g, with an average value of 0.31 mg/g. The maximal concentration was exceeding MAC by 18 times. High sulphur concentrations observed in the bottom sediments of the Kerch Strait in 2008 had most likely directly resulted from the Kerch Strait accident on 11 November 2007.

### 7.2.2. UA: MHI. Pollutants present in the water and bottom sediments in December 2007 and March 2008

MHI NASU (Sevastopol) conducted on 6–9 December 2007 and in March 2008 two expeditions to study pollution of the water and bottom sediments of the Kerch Strait (map of stations is given in Subchapter 6.1: Fig. 6.1.7a). Petroleum hydrocarbons (Chapter 6), chlorinated hydrocarbons and trace metals were investigated during that study.

#### 7.2.2.1. Chlorinated hydrocarbons

**7.2.2.1.1. Water column.** In December 2007, the chlorinated pesticides concentration in the surface layer was varying in a wide range (Table 7.2.2a).

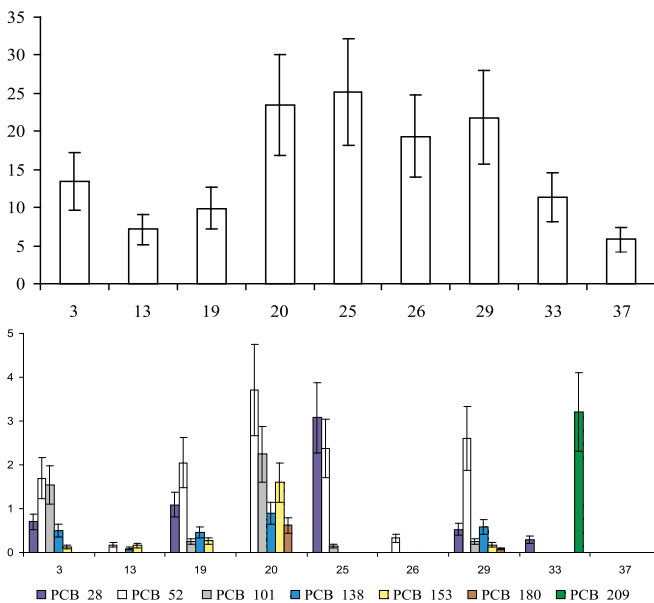
Table 7.2.2a. Chlorinated hydrocarbons concentration (ng/l) in the Kerch Strait surface waters in December 2007.

Parameter, ng/l	Range	Average	Maximal values location
Lindane	0.003–2.52	0.58	vicinity of the Tuzla Island
Heptachlor	3.55–10.23	6.93	the Kerch Strait entrance to the Azov Sea
pp-DDT	1.10–12.19	5.00	the Kerch Strait central part
pp-DDE	1.48–4.34	2.64	
pp-DDD	0.24–4.37	2.61	

All chlorinated pesticides had formed rather high concentrations that were often exceeding the maximum allowed quantity (Fig. 7.2.2a).

Within the area under review, concentrations of all investigated individual PCBs were lower than 4 ng/l (Fig. 7.2.2b), whereas the MAC is 10 ng/l.

In March 2008,  $\gamma$ -HCH (lindane) and all forms of DDT group were registered in the Kerch Strait (Table 7.2.2b). Pollutants concentration recorded was 5–20 times lower than in December 2007.



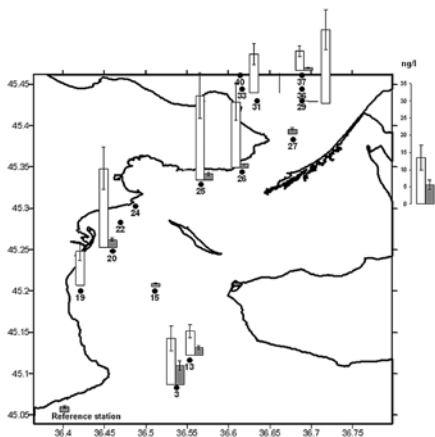
**Fig. 7.2.2a.** The total chlorinated pesticides concentration (ng/l) in the Kerch Strait surface waters on 6–9 December 2007. The station numbers are given at axis x, see also Fig. 6.1.7a.

**Fig. 7.2.2b.** PCBs concentrations (ng/l) in the Kerch Strait surface waters on 6–9 December 2007. The station numbers are given at axis x, see also Fig. 6.1.7a.

**Table 7.2.2b.** Chlorinated pesticides concentration (ng/l) in the Kerch Strait surface waters in March 2008.

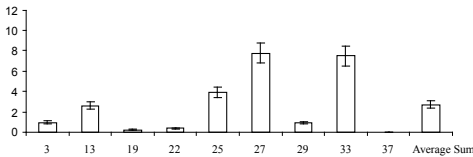
Parameter, ng/l	Range	Average	Maximal values location
Lindane	0.04–0.25	0.11	by the Tuzla Island Western end
Heptachlor	0.12–0.73	0.37	–
DDT	0.18–1.13	0.57	by the Tuzla Island Western end
DDE	0.04–3.65	0.57	the Kerch Strait Southern entrance to the Black Sea
DDD	0.08–2.64	0.67	
PCBs	0.00–2.00	1.09	the Kerch Strait Southern entrance to the Black Sea

In March 2008, PCBs concentration was rather low and within 2 ng/l, while the average value was 1.09 ng/l. That corresponded to the «unpolluted water» quality class according to the World Health Organization, WHO (1980) classification. The individual congeners # 52, # 101, # 138, # 153 and # 180 were distributed rather unevenly within the studied area and their concentration was significantly lower than in December 2007 (Fig. 7.2.2c).



**Fig. 7.2.2c.** Distribution of PCBs (ng/l) in the Kerch Strait surface waters in December 2007 (white) and in March 2008 (grey).

**7.2.2.1.2. Bottom sediments.** In December 2007, the chlorinated pesticides content in the Kerch Strait sediments was insignificant and was as low as 1.84 ng/g and 1.57 ng/g at two out of eight stations observed (Stations 19 and 22 accordingly, central part of the Strait). PCBs were present at all stations though in low concentration. Within that class of pollutants, the congeners #138 (from 0.11 to 1.69 with the average of 0.84 ng/g) and #153 (0.13–2.39, the mean was 1.16 ng/g) were distributed wider. The PCBs total concentration was reaching the levels of 7.78 ng/g at Station 27 and 7.51 ng/g at Station 33 at the Kerch Strait Northern entrance (Fig. 7.2.2d), and those levels were about 3 times lower the permitted concentration of 20 ng/g (Warner H., van Dokkum R., 2002, «Niederlandische Liste») accepted as a norm for the Black Sea sediments.



**Fig. 7.2.2d.** PCBs (ng/g) total concentration per station in the Kerch Strait bottom sediments on 6–9 December 2007.

The polychlorobiphenyls spatial distribution in both the water column and the bottom sediments was characterized by the elevated concentrations present in the Kerch Strait middle part and in the vicinity of the Kerch port (at Station 20), as well as at the Northern entrance stations (Station 27 and Station 33). Those areas were quite close to the boat routes and presence of various pollutants discharged by the vessels on random, during the maintenance or resulting out of small accidents was typical for them.

In March 2008, chlorinated pesticides from the DDT group were detected in the sediments at all stations. DDT was dominating in comparison with its metabolites whose presence was taken for a sign of the pesticides fresh input into the ecosystem. Among the seven tested individual PCBs, the congeners #101, #138, #153, #180 and #209 were found in the bottom sediments and their average concentration was registered as 3.06 ng/g (Emelianov V.A. *et al*, 2004), nearly 7 times lower the PC of 20 ng/g.

### 7.2.2.2. Trace metals<sup>1</sup> in bottom sediments

An important source of trace metals in the Kerch Strait are the ports, moorages, coastal industrial and municipal installations, as well as certain dumping sites located close to the Kerch Strait entrance (Petrenko O.A., Sebah L.K., Fashchuk D.Ya., 2002; Zhugailo S.S., Petrenko O.A., 2009).

On 6–9 December 2007, the most common trace metals concentrations in the Kerch Strait bottom sediments were registered below the Detection Limit of  $\text{Cu} < 20 \cdot 10^{-4}\%$ ,  $\text{Co} < 10 \cdot 10^{-4}\%$ ,  $\text{Pb} < 25 \cdot 10^{-4}\%$  and  $\text{As} < 20 \cdot 10^{-4}\%$ . As for Ni, Co, Fe, Cr, V and As, local patches were recorded having these metals in rather high concentrations. Most probably the bottom sediments granulometric and chemical composition (for example, the percentage of muddy particles or organic matter), and the water circulation were the most important factors for formation of such local patches.

In March 2008, the trace metals spatial distribution was following their pattern observed in winter (Fig. 7.2.2e). Significant gradients of concentrations across the Kerch Strait were typical for all metals revealing extreme values at the central axis line of Cr (Fig. 7.2.2e) and within the coastal zone of Sr (Fig. 7.2.2f).

<sup>1</sup> There were no measurements of trace metals in water

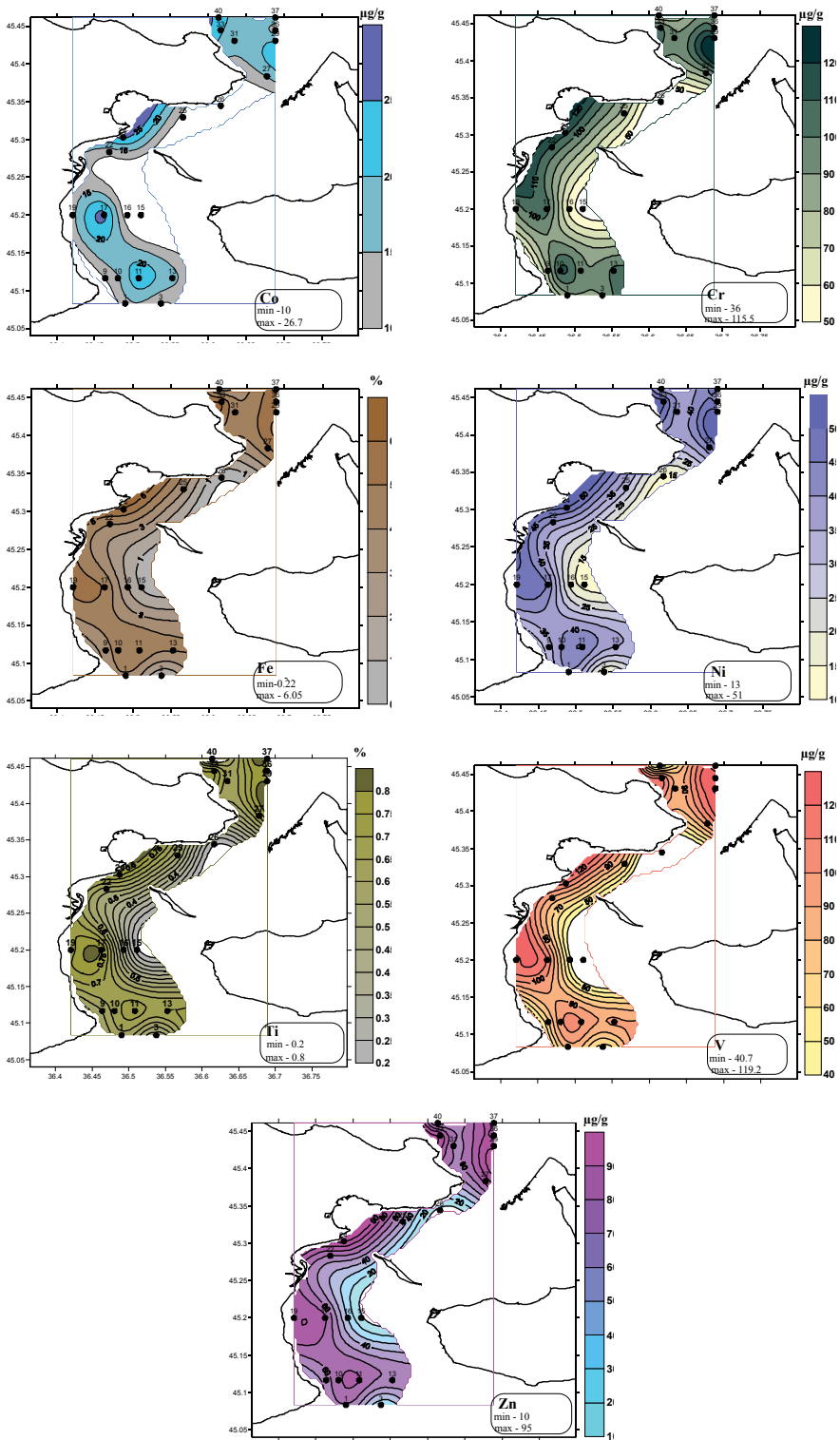
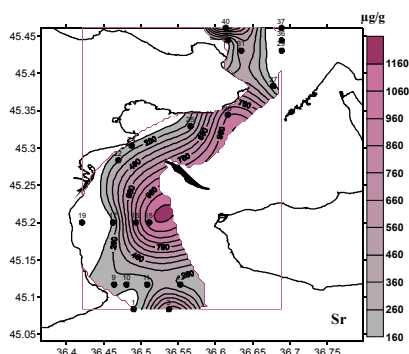


Fig. 7.2.2e. Various trace metals ( $\mu\text{g/g}$ ) spatial distribution in the Kerch Strait bottom sediments in March 2007.

The patchiness of trace metals is largely formed by the Kerch Strait dominant currents and the size spectrum of the bottom sediments particles, as mentioned above. Spring distributions of chromium (av. 93  $\mu\text{g/g}$  and max. 115.5  $\mu\text{g/g}$ ) and zinc (av. 61  $\mu\text{g/g}$  and max. 95  $\mu\text{g/g}$ ) were similar, with maxima registered in the Kerch Strait Northern part. It was revealed that concentrations had decreased slightly moving southwards and significantly in the central zone. Zinc distribution presented much more patchiness than the chromium. The mean content of nickel in the bottom sediments was 29.14  $\mu\text{g/g}$  and the maximum of 50.0  $\mu\text{g/g}$  was recorded in the Kerch Strait Northern coastal part. The maximal value was exceeding its average by 72% indicating patchiness in the nickel distribution. The nickel general concentration in the Kerch Strait bottom sediments was rather low and close to background levels of unpolluted areas.

Titanium and iron distributions were similar revealing their minimal quantities in the Kerch Strait central part and high concentrations within the coastal zone. The mean concentration of titanium oxide was 0.6% and the maximum — 0.78%, while for the iron oxide those concentrations were 3.78% and 6.05% respectively. Their quantities content was similar to the registered for the Black Sea shelf unpolluted areas.

Unlike other metals, strontium was concentrated in the central part of the Kerch Strait (Fig. 7.2.2f) and its mean level was 366.25  $\mu\text{g/g}$  and the maximal quantity — 1125  $\mu\text{g/g}$ . The mean and maximal values ratio was exceeding 200% that could be interpreted as evidence of the metal patchy distribution.



**Fig. 7.2.2f.** Strontium ( $\mu\text{g/g}$ ) distribution in the Kerch Strait bottom sediments in March 2008.

### 7.2.3. UA: UkrSCES. July and December 2009, the Kerch Strait (the V. Parshin RV 30<sup>th</sup> and 31<sup>st</sup> cruises)

#### 7.2.3.1. Chlorinated hydrocarbons in bottom sediments

In July and December 2009, respectively, 12 and 23 samples of bottom sediments were collected for analysis of the chlorinated pesticides and polychlorinated biphenyls content. The average concentrations of individual pesticides in sediments did not exceed 1 PC (Tab. 7.2.3a, Tab. 7.2.3b, Fig. 7.2.3a).

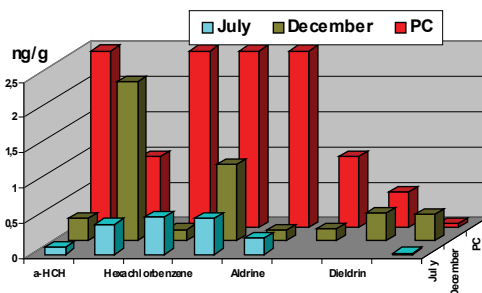
**Table 7.2.3a.** Statistical characteristics of the chlorinated pesticides concentration in the Kerch Strait bottom sediments on 8 July 2009 (the V. Parshin RV 30<sup>th</sup> cruise). In **bold** the numbers exceeding 1 PC are marked.

Pesticides, ng/g	$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH (Lindane)	HCB	Heptachlor	Aldrine
Average value	0.11	0.43	0.02	0.53	0.52	0.24
Minimum	<0.05	<0.05	0.02	<0.05	<0.05	<0.05
Maximum	0.74	<b>3.22</b>	0.02	0.70	<b>5.12</b>	1.59
PC	2.5	1.0	0.05	2.5	2.5	2.5



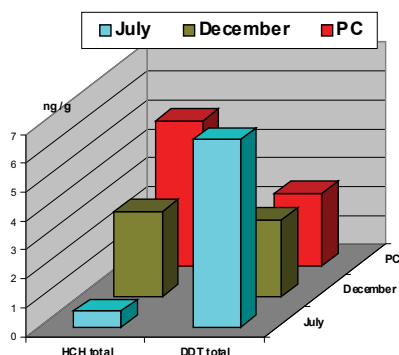
**Table 7.2.3b.** Statistical characteristics of the chlorinated hydrocarbons concentration in the Kerch Strait bottom sediments on 8–11 December 2009 (the *V. Parshin* RV 31<sup>st</sup> cruise). In **bold** the numbers exceeding 1 PC are marked.

Pesticides, ng/g	$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH (Lindane)	HCB	Heptachlor	Aldrine	Endrin	Dieldrin
Average value	0.32	<b>2.25</b>	<b>0.37</b>	0.16	1.08	0.15	0.17	0.40
Minimum	0.10	0.88	0.12	0.10	0.10	<0.05	<0.05	0.11
Maximum	0.62	<b>3.68</b>	<b>0.66</b>	0.32	<b>7.34</b>	0.80	<b>2.08</b>	<b>0.83</b>
PC	2.5	1.0	0.05	2.5	2.5	2.5	1.0	0.5



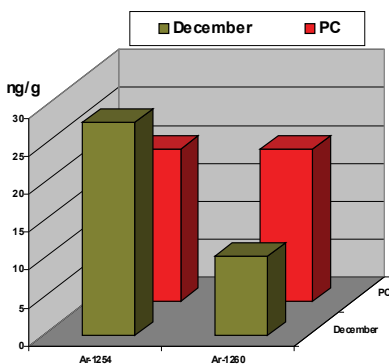
**Fig. 7.2.3a.** Average concentration of chlorinated pesticides in the bottom sediments of the Kerch Strait in 2009.

The exception was for lindane and its  $\beta$ -isomer, their average concentrations in December 2009 exceeded PC, but the average concentration of the sum of hexachlorocyclohexane isomers was below 1 PC (Fig. 7.2.3b). The average level of DDT and its metabolites in this study area in 2009 was above the prescribed standard.



**Fig. 7.2.3b.** Average concentration of sums of DDT and HCH in the bottom sediments of the Kerch Strait in 2009.

Amount of PCBs in relation to the standards of Ar-1254 and Ar-1260 were determined in December 2009. The results indicated a fairly high level of accumulation of those toxic compounds in bottom sediments of the Kerch Strait (Fig. 7.2.3c).



**Fig. 7.2.3c.** Average concentrations of total PCBs in the bottom sediments of the Kerch Strait in 2009.

### 7.2.3.2. Trace metals

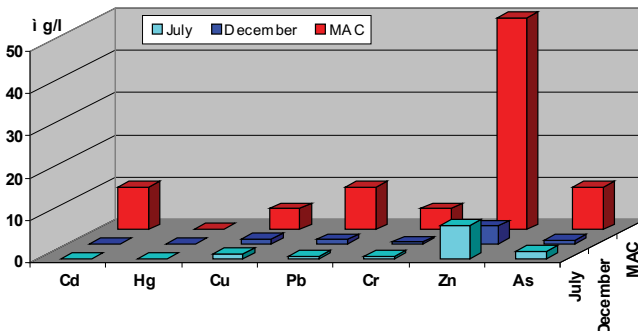
**7.2.3.2.1. Water column.** In 2009, observations were carried out at 8 stations in July and 25 stations in December (see a map of stations in Chapter 5, Fig. 5.2.5.1a and Fig. 5.2.5.2b) and they revealed the trace metals presence in concentrations almost ten times lower than MAC (Tab. 7.2.3c and d, Fig. 7.2.3d).

**Table 7.2.3c.** Statistical characteristics of Trace metals ( $\mu\text{g/l}$ ) in the Kerch Strait surface waters on 8 July 2009.

Trace metals, $\mu\text{g/l}$	Cd	Hg	Cu	Pb	Cr	Zn	As
Average value	0.07	0.01	1.2	0.6	0.6	7.8	1.8
Minimum	0.05	0.01	0.5	0.5	0.5	1.1	1.0
Maximum	0.10	0.019	2.4	0.9	0.8	15.3	3.1
MAC	10	0.1	5	10	5	50	10

**Table 7.2.3d.** Statistical characteristics of trace metals ( $\mu\text{g/l}$ ) in the Kerch Strait surface waters in December 2009.

Trace metals, $\mu\text{g/l}$	Cd	Hg	Cu	Pb	Cr	Zn	As
Average value	0.06	0.01	1.3	1.1	0.5	4.3	1.0
Minimum	0.05	0.01	0.4	1.0	0.5	1.2	1.0
Maximum	0.13	0.01	3.4	1.9	0.5	13.8	1.0
MAC	10	0.1	5	10	5	50	10



**Fig. 7.2.3d.** Trace metals concentration in the surface waters of the Kerch Strait in 2009.

**7.2.3.2.2. Bottom sediments.** The bottom sediments samples were taken at 12 stations in July and 23 stations in December 2009 and the trace metals content detected therein was largely lower 1 MAC. In a couple of cases in July only nickel, copper and chromium were exceeding the MAC values (Tab. 7.2.3e). The metals content in the bottom sediments was within the typical range for the region.

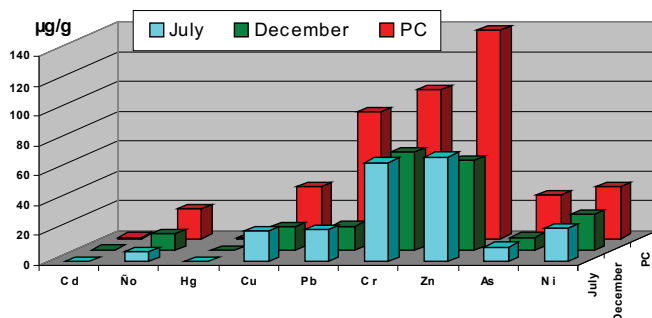
**Table 7.2.3e.** Statistical characteristics of the trace metals concentration in the Kerch Strait bottom sediments on 8 July 2009 (the *V. Parshin* RV 30<sup>th</sup> cruise). In **bold** the numbers exceeding 1 PC are marked.

Trace metals, $\mu\text{g/g}$	Cd	Co	Hg	Cu	Pb	Cr	Zn	As	Ni
Average value	0.130	6.4	0.036	20.5	21.7	66.6	70.2	9.8	22.0
Minimum	0.063	3.0	0.011	4.8	14.9	16.3	32.8	4.4	10.8
Maximum	0.226	10.4	0.056	<b>55.6</b>	30.7	<b>108</b>	111	14.7	<b>40.3</b>
PC	0.8	20	0.3	35	85	100	140	29	35

Trace metals investigated in December 2009 revealed the presence of cadmium, cobalt, mercury, copper, lead, chromium, zinc, arsenic, nickel and aluminum. The chromium and nickel maxima were slightly exceeding the norms (Tab. 7.2.3f), while the average values during 2009 were significantly lower (Fig 7.2.3e).

**Table 7.2.3f.** Statistical characteristics of the trace metals concentration in the Kerch Strait bottom sediments on 8–11 December 2009. In **bold** the numbers exceeding 1 PC are marked.

Trace metals, $\mu\text{g/g}$	Cd	Co	Hg	Cu	Pb	Cr	Zn	As	Ni
Average value	0.147	10.7	0.032	15.7	16.1	65.9	60.4	8.6	23.7
Minimum	0.090	3.1	0.010	3.2	7.6	15.7	19.0	4.4	7.1
Maximum	0.262	17.2	0.066	31.8	28.2	<b>112</b>	120	23.5	<b>43.1</b>
PC	0.8	20	0.3	35	85	100	140	29	35



**Fig. 7.2.3e.** Trace metals concentration in the bottom sediments of the Kerch Strait in 2009.

#### 7.2.4. UA: IBSS. Pollutants present in the water and bottom sediments in December 2007 and December 2009

To determine organochlorine compounds, mercury and long-lived radionuclides in the water and bottom sediments, the IBSS Department of Radiation and Chemical Biology collected samples at ten stations of the Kerch Strait region on 16 December 2007 (the map of stations is shown in Subchapter 6.2, Fig. 6.2.4a). IBSS carried out the next Kerch Strait expedition during December 2009 and studied the chlorinated organics concentration present in the bottom sediments.

##### 7.2.4.1. Chlorinated hydrocarbons

The polychlorinated biphenyls (PCBs) contaminants originating sources is industrial activity like ship exploitation and maintenance within the Kerch Bay and in the Kerch Strait, while organochlorine pesticides (DDTs) come from agriculture (Fedorov, 1999; Li *et al.*, 2006). The organochlorine compounds concentration was measured in the surface sea waters (December 2007) and in the bottom sediments surface layer (0–5 cm), (December 2007 and December 2009). The organochlorine pesticides and PCBs analysis was conducted according to the standard methods applicable (Oradovsky S. G., 1993, *Methodic Guidelines: Detection of pollutants in bottom sediments samples and on suspended solids*, 1996). The organochlorine residues quantification was done through using the Varian 3800 gas chromatograph equipped with the  $^{63}\text{Ni}$  electron capture detector and capillary column. The measurement errors were estimated as 15% of the bottom sediment samples and as 28% of the water samples. The quality assurance criteria were applied prior to the samples analysis. The inter-comparison exercises undertaken in the frameworks of the International Atomic Energy Agency Program (MESL/IAEA-159, 2007) have given satisfactory results.

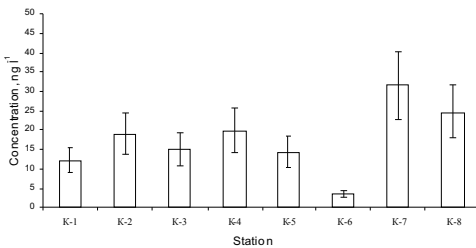
**7.2.4.1.1. Surface water.** In December 2007, DDT and metabolites were determined present in water at six stations. The pesticides concentrations varied in the range of 1.26–4.07 ng/l, while 1 MAC was equal 10 ng/l (Tab. 7.2.4a).

**Table 7.2.4a.** DDTs and PCBs concentrations in the Kerch Strait surface waters in December 2007.

Organochlorine compounds	Stations							
	K-1	K-2	K-3	K-4	K-5	K-6	K-7	K-8
	organochlorine pesticides, ng/l							
p, p'- DDE	–	–	–	–	3.55	–	2.94	1.80
p, p'- DDD	1.26	2.47	–	–	–	–	–	–
p, p'- DDT	2.87	4.07	–	–	–	2.60	–	–
	polychlorinated biphenyls, ng/l							
# 28	4.86	3.71	1.03	0.56	2.42	1.45	5.74	–
# 52	3.79	6.32	0.13	7.65	4.57	–	8.93	8.81
# 101	1.73	4.68	2.70	2.08	5.51	0.75	2.41	2.74
# 138	0.96	1.81	4.48	5.68	0.76	1.29	3.76	3.95
# 153	0.85	2.49	6.76	1.58	1.09	–	3.94	5.16
# 180	–	–	–	2.21	–	–	5.59	1.44
# 209	–	–	–	0.20	–	–	1.10	2.55
ΣPCBs	12.18	19.00	15.10	19.97	14.34	3.50	31.46	24.65

Note: «–» mean below Detection Limit

For the PCBs pollution indicators, seven congeners suggested by the International Council for Exploration of the Sea, i. e., ## 28, 52, 101, 118, 138, 153 and 180 (Duinker *et al.*, 1988) were selected. In December 2007, polychlorinated biphenyls (PCBs) high content was registered in the Kerch Strait surface waters. Total concentrations of seven PCBs congeners (## 28, 52, 101, 138, 153, 180 and 209) varied from 3.50 ng/l to 31.46 ng/l and exceeded 3 MAC (Tab. 7.2.4a and Fig. 7.2.4a). That could be attributed to forbidden boat fuel tanks washing and ballast waters discharges or directly linked to the vessels sunk in the result of the storm in November 2007.



**Fig. 7.2.4a.** The PCBs congeners total concentration in the Kerch Strait surface waters in December 2007.

**7.2.4.1.2. Bottom sediments.** In December 2007, the PCBs presence was determined in the bottom sediments at all stations, but in low concentration. Their content ranged from 0.41 ng/g to 1.39 ng/g of dry weight and those levels were much lower 1 PC of 20 ng/g (Warmer H., van Dokkum R., 2002, «Niederlandische Liste»), (Tab. 7.2.4b). The PCBs concentration in the Kerch Strait bottom sediments was substantially lower in comparison to the IBSS indicators obtained at the Sevastopol and Balaklava Bights, as well as at the Feodosiya harbor.

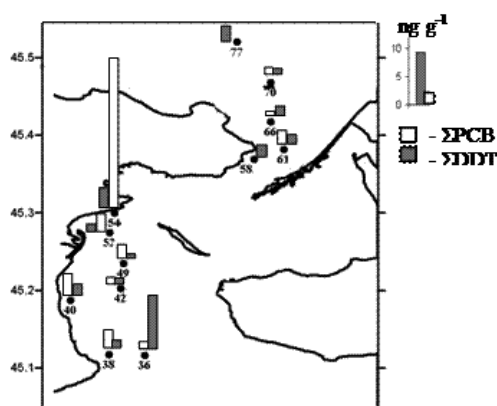
**Table 7.2.4b.** DDTs and PCBs concentrations in the Kerch Strait bottom sediments in December 2007.

Organochlorine compounds	Stations									
	K-1	K-2	K-3	K-4	K-5	K-6	K-7	K-8	K-9	K-10
	organochlorine pesticides, ng/g of dry weight									
p,p'- DDE	0.69	0.61	0.72	1.35	0.19	0.12	0.42	1.05	0.37	0.49
p,p'- DDD	0.22	0.09	0.68	1.43	0.11	0.80	0.49	2.12	0.69	27.69

p,p'- DDT	–	–	0.31	2.15	0.54	–	0.44	–	–	–
ΣDDT	0.91	0.7	1.71	4.13	0.84	0.92	1.35	3.17	1.06	28.18
	<b>polychlorinated biphenyls, ng/g of dry weight</b>									
# 101	0.50	0.27	0.09	0.74	0.06	0.20	0.27	0.39	0.05	0.20
# 138	0.03	0.12	0.11	0.03	0.04	0.13	0.25	0.05	0.28	0.10
# 153	0.30	0.21	0.19	0.35	0.10	0.44	0.37	0.58	0.57	0.32
# 180	0.06	–	0.02	–	0.04	0.15	0.16	0.11	–	0.07
# 209	–	–	–	–	0.08	0.09	0.11	0.27	–	–
ΣPCBs	0.89	0.60	0.41	1.12	0.33	1.01	1.16	1.39	0.89	0.69

Note: «–» mean below Detection Limit

In December 2009, the DDT group organochlorine pesticides and five PCBs congeners (## 101, 138, 153, 180 and 209) were found present in the Kerch Strait sediments at all stations (Fig. 7.2.4b). DDE and DDD dominated in comparison with DDT. Total concentrations of five PCBs congeners (## 101, 138, 153, 180 and 209) ranged from 0.43 ng/g of dry weight to 23.56 ng/g, while their maximum was exceeding permissible concentrations. Their averaged concentration equaled 2.14 ng/g of dry weight, while its minimum was detected in the sandy sediments. In general, the PCBs registered concentration was significantly higher than two years earlier, whereas the DDTs pesticides levels were about three times lower.



**Fig. 7.2.4b.** The sampling sites location and distribution of total PCBs (white bars) and total DDTs (grey bars) in the Kerch Strait bottom sediments in December 2009.

#### 7.2.4.2. Trace metals (mercury)

**7.2.4.2.1. Surface water.** The mercury concentration maximum (15.43 ng/l) measured in the Kerch Strait surface waters in December 2007 (Tab. 7.2.4c) slightly exceeded (by 15 %) the maximal allowed concentration (MAC List, 1999). That level was substantially lower in comparison with the IBSS detected levels in 1999–2004 for the same region, i. e., 62–80 ng/l in the surface waters and 20–28 ng/l in the near bottom waters with predomination of dissolved mercury (Kostova S. K., Popovichev V. N., 2002).

**7.2.4.2.2. Bottom sediments.** Mercury concentration in the Kerch Strait bottom sediments in December 2007 varied from 2.3 ng/g to 9.8 ng/g of dry weight (Tab. 7.2.4c). Those concentrations were considerably lower in comparison with the usually acceptable mercury natural maximal content for the shelf bottom sediments (100 ng/g

of dry weight) and definitely much lower its norm of 300 ng/g (Warmer H., van Dokkum R., 2002).

**Table 7.2.4c.** Mercury concentrations in the Kerch Strait surface waters, suspended solids and bottom sediments in December 2007.

Station	Water, ng/l			Particles, ng/g of dry weight	Bottom sediments, ng/g	
	Dissolved phase	Particles phase	Total		Wet weight	Dry weight
K-1	1.0	2.38	3.38 ± 0.22	9.50 ± 1.29	2.56 ± 0.35	6.94 ± 0.94
K-2	2.0	13.43	15.43 ± 0.99	60.80 ± 8.27	3.46 ± 0.47	9.80 ± 1.34
K-3	6.0	2.90	8.90 ± 0.57	11.79 ± 1.60	4.37 ± 0.59	9.40 ± 1.28
K-4	2.0	3.46	5.46 ± 0.35	14.38 ± 1.96	1.98 ± 0.27	2.28 ± 0.31
K-5	3.0	0.24	3.24 ± 0.22	0.87 ± 0.12	1.85 ± 0.27	2.63 ± 0.36
K-6	1.0	5.45	6.45 ± 0.40	44.76 ± 6.10	2.92 ± 0.40	7.59 ± 1.00
K-7	3.0	1.72	4.72 ± 0.30	11.08 ± 1.51	2.67 ± 0.36	6.27 ± 0.85
K-8	1.0	3.20	4.20 ± 0.27	15.00 ± 2.00	3.25 ± 0.44	7.80 ± 1.10
K-9	–	–	–	–	2.47 ± 0.34	6.40 ± 0.87
K-10	–	–	–	–	2.24 ± 0.30	8.15 ± 1.10

Note: «–» mean below Detection Limit.

### 7.2.4.3. Long-lived radionuclides

The  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  anthropogenic long-lived radionuclides have primarily originated from the large-scale atmospheric nuclear weapon tests conducted prior to the 1963 test-ban treaty conclusion. The Chernobyl Nuclear Power Plant (NPP) Accident in April 1986 contributed additional direct radioactive contamination through their fallouts onto the Black Sea surface and indirect contamination through atmospheric release and deposition of radionuclides on the drainage basin with the further runoff to enter into the sea. (Polikarpov G. G. *et al.*, 2008). It should be noted that  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  are the especially conservative elements while in the marine environment, but those radionuclides could reveal considerable sedimentation in the coastal and estuarine zones.

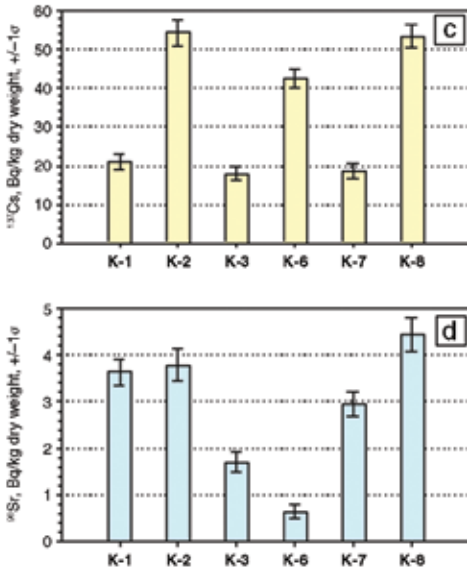
The gamma spectrometric measurements of  $^{137}\text{Cs}$  activities in the bottom sediment samples were made by using a high-purity germanium (HPG), ORTEC GMX-10 detector and the reference samples obtained from the IAEA Monaco Marine Environmental Laboratory. Determination of  $^{90}\text{Sr}$  activities in the bottom sediment samples was carried out in compliance with the chemical procedure described accordingly (Harvey B. K. *et al.*, 1989) and following up on the measurements made through using the *Quantulus-1220* ultra low-level liquid scintillation beta-counter.

The  $^{137}\text{Cs}$  activity in the Kerch Strait bottom sediments in December 2007 varied from 18 Bq/kg to 54 Bq/kg of dry weight (Fig. 7.2.4c) and was partially dependent on the bottom sediments composition. The  $^{137}\text{Cs}$  maximal concentrations in the Kerch Strait bottom sediments were less essential in comparison with the IBSS levels registered in 1998–2000 in the Dnieper and Danube Rivers estuarine zones, i. e., ~ 150 Bq/kg and 250–300 Bq/kg of dry weight respectively (Gulin S. B. *et al.*, 2002).

The  $^{90}\text{Sr}$  activity in the Kerch Strait bottom sediments in December 2007 was considered negligible, i. e., ~ 0.6 Bq/kg — 4.4 Bq/kg of dry weight (Fig. 7.2.4d), in comparison with the 1997–2000 IBSS registered levels of ~ 150 Bq/kg of dry weight that

were close to the levels produced by the  $^{90}\text{Sr}$  main source of discharge into the Black Sea after the Chernobyl NPP accident, i. e., of the Dnieper River (Mirzoeva N. Yu. *et al.*, 2005).

Up till now the  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  long-lived radionuclides local sources at the Black Sea and the Kerch Strait specifically remain undiscovered.



**Fig. 7.2.4c, d.** The  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  activities in the Kerch Strait bottom sediments in December 2007.

### 7.3. Hydrochemical Index of Water Pollution (IWP)

Water Quality Zoning of the area studied was done by ChAD (Novorossiysk). It was based on the water pollution complex index (IWP) calculated through using the data provided by several 2008 expeditions assigned with a task of carrying out an ecological assessment of the Kerch Strait, and the Black and Azov Seas marine environment condition status after the 11 November 2007 shipwreck (see Chapter 6.1.12). IWP was calculated for different seasons, as well as for the surface and bottom layers. For IWP calculating, besides the compulsory dissolved oxygen values (MinAC 6.0 mg/l), those of the phosphates (MAC 0.15 mg/l), ammonia (MAC 2.9 mg/l) and petroleum hydrocarbons (MAC 0.05 mg/l) concentrations were used as well.

IWP is the index most frequently applied by the former Soviet Union countries for the marine water quality assessment (MR, *Methodological recommendations...*, 1988). It uses the average concentration values of a limited number of the most important pollutants for the area in question. For marine waters, four parameters are considered and IWP is calculated as:

$$\text{IWP} = \sum_{i=1}^4 \frac{C_i}{\text{MAC}_i} / 4$$

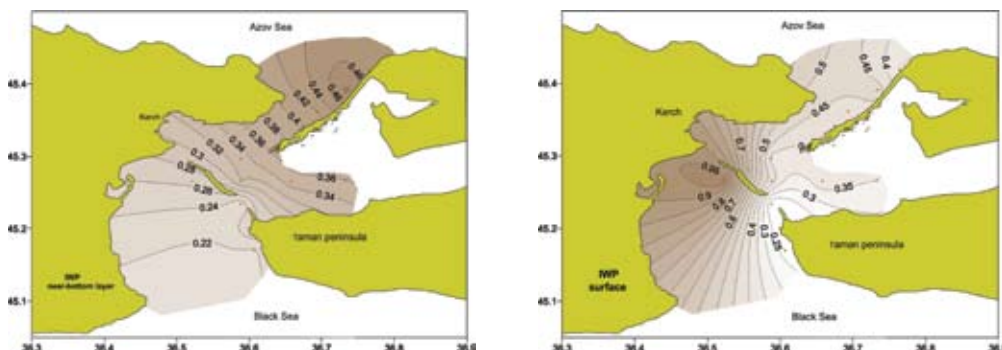
where  $C_i$  is concentration of three major pollutants and dissolved oxygen. This concentration is divided by the Maximum Allowed Concentration. Thus, the marine environment index is calculated as an average of 4 indicators, i. e., of oxygen and three pollutants that are quite likely to exceed the maximum allowed concentration. A con-

stant parameter present in this calculation is the dissolved oxygen value. The water bodies quality is unitized into classes depending upon the IWP value (Table 7.3a).

**Table 7.3a.** The water quality classes based on a complex Index of Water Pollution (IWP).

Water quality classes		IWP range
very clean	I	IWP < 0.25
clean	II	0.25 < IWP ≤ 0.75
moderately polluted	III	0.75 < IWP ≤ 1.25
polluted	IV	1.25 < IWP ≤ 1.75
dirty	V	1.75 < IWP ≤ 3.00
very dirty	VI	3.00 < IWP ≤ 5.00
extremely dirty	VII	IWP > 5.00

Based on the information provided by the ChAD expeditions, the IWP calculated value varied from 0.19 to 5.66. Thus, the Kerch Strait waters were characterized by a large spread of IWP values varying from the 1st to the 7<sup>th</sup> class of water quality in the range from ‘clean’ to ‘extremely dirty’. The case of August 2008 was taken as an example (Fig 7.3a).



**Fig. 7.3a.** The IWP distribution at the surface (left) and in the bottom (right) layers on 31 August 2008.

In the period of the summer survey, IWP varied from 0.2 to 0.99 that corresponded to the 1st-3rd classes of water quality. Basically, the IWP average values varied for different expeditions and layers in the range of 0.28–0.73 (Table. 7.3b). Those values corresponded to a clean type of water or its 2<sup>nd</sup> class (MR, 1988). The bottom layer was cleaner than the surface one. In general, throughout the water column, the more polluted areas were detected in the Western and Northern parts of the Kerch Strait.

**Table 7.3b.** The IWP variability statistics based on the ChAD surveys carried out on the Kerch Strait in 2008.

	No of stations	min	max	Average	Standard deviation
surface layer, summer, July–August	11	0.20	0.99	0.40	0.21
bottom layer, summer, July–August	11	0.22	0.48	0.33	0.09
surface layer, autumn, November	31	0.19	0.46	0.28	0.07
bottom layer, autumn, November	31	0.19	0.64	0.29	0.12
surface layer, winter, December	28	0.19	5.66	0.73	1.34
bottom layer, winter, December	28	0.19	1.53	0.38	0.29

The IWP maximum values corresponding to waters of extremely dirty types were detected in the Southern part of the Kerch Strait during the winter period. Those high IWP values had derived from petroleum hydrocarbons high concentrations present therein.



#### **7.4. Summary: Other pollutants in the Kerch Strait**

Prior and especially after the November 2007 heavy storm, frequent investigations were carried out to define pollutants distribution in the Kerch Strait area. The trace metals 1990s historical data have revealed presence in the bottom sediments of numerous geochemical elements with concentrations at the background level. Sometimes elevated cadmium, zinc and iron content were observed. Constant high arsenic values had probably derived from anthropogenic pollution and an increased natural geochemical background. The measurements performed straight after the Kerch Strait accident, i. e., in December 2007 and March 2008 revealed the maximal levels of chromium, cobalt, zinc and nickel in sediments reaching about 0.7–1.6 PC and the much lower average values. A year later in July 2009, in three cases only the copper, chromium and nickel concentrations in sediments were detected slightly above 1 PC, while for the others (Cd, Co, Hg, Pb, Zn, As and Al) they were substantially lower than the mentioned threshold. At the same time, results were obtained for the strait waters and all the metals concentrations there tested on 8 July 2009 sustained less than 1 MAC (approximately ten times lower). Some increase of the metals content in the bottom sediments was recorded in December 2009 when maximum concentrations of chromium and nickel had slightly exceeded 1 PC, while those for cadmium, mercury, cobalt, copper, zinc and arsenic were slightly less than the norm. In general, metal content in the Kerch Strait area before and after the accident in November 2007 was at the geochemical background level and was exceeding the norm occasionally only.

Sulphur concentration in the Kerch Strait bottom sediments was detected very high through the whole year after the November 2007 shipwreck accident. Average concentrations during summer, autumn, and winter 2008 were registered as 3.25, 1.3, and 1.67 of PC respectively and their maximum had reached 2.87 mg/g. Nevertheless, no apparent negative impact on the nature was recorded most probably due to the substance low poisoning features.

Chlorinated pesticides in the Kerch Strait waters were detected rather often and were sometimes exceeding the MAC. All forms of the HCH and DDT group were registered including «fresh» lindane and DDT. For instance, in December 2007 the  $\gamma$ -HCH maximum concentration was reaching 2.5 ng/l (0.25 MAC) and that of DDT — 12.2 ng/l (1.2 MAC), (MHI results). A similar level (1.3 ng/l — 4.0 ng/l) was recorded about the same time by another Institution (IBSS). In a couple of months their concentration in the water went down by about 10 times (MHI), which was evidence of a temporal variability of a high level to have probably resulted from arrival to the Kerch Strait of the waters of different origin (e. g., washing of pesticides from agricultural lands after heavy rains, etc.).

In December 2007 and March 2008, the total pesticides concentration in the bottom sediments was registered low and not exceeding 2 ng/g (MHI). An year later by July 2009 their content had increased significantly, especially of DDE that got the 7.5 ng/g maximum, and rather often exceeded the PC (UkrSCES). Such a discrepancy in DDE values could be to some extent explained by the analytical differences existing between the two Ukrainian institutions UkrSCES and MHI providing data.

The data on PCBs presented by different Institutes do not allow to draw conclusions on the level of this kind of pollution in the Kerch Strait. For instance, one

source (MHI NASU) has reported rather low polychlorobiphenyls quantity present in the Kerch Strait bottom sediments. Their total concentration was given as reaching 7.78 ng/g in December 2007 and that level was about three times lower the Permissible Concentration. Some months later (spring 2008) their average content was registered even lower as 3.06 ng/g and the situation has not changed in July 2009. Still, the December 2009 wide investigation results of UkrSCES showed all the tested sites strongly polluted with PCBs at the level reaching up to 20 PC.

Results obtained from the water studies were also with some discrepancies. Thus, in general, according to the investigations described above, a low PCBs content in winter 2007 and spring 2008 was observed in the Kerch Strait by MHI. That level corresponded to «unpolluted water» in line with the World Health Organization classification. Unlike, the investigations carried out by IBSS in December 2007 revealed the PCBs presence in the Kerch Strait surface waters as high as 31.46 ng/l (MAC is 10 ng/l). Contradictions in data provided by different analytical laboratories could appear because of various reasons, of course. Different sampling procedures and methodologies of processing applied could serve as a possible explanation for disparities in the PCBs data. Lack of normalization, absence of parallel granulometric analysis should also be mentioned among the possible sources of discrepancies. Inventories of the applied methodologies and equipment used should be kept in parallel with the reported data. Inter-calibration and inter-comparison exercises should be undertaken in the Black Sea region for both water and sediments to make sure that the levels of PCBs measured reflect the real intensity of this kind of pollution in the studied marine environments.

The complex index of water pollution (IWP) was applied by the former Soviet Union countries as a standard tool for the water quality classification within the studied area. Based on average calculation, the Kerch Strait waters could be assessed as conditionally «clean» or «moderately polluted» during 2007–2009, while the maximal levels observed have revealed certain periods and places heavily polluted by petroleum hydrocarbons.