Subchapter 6.2. Bottom sediments

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Trace of the long-present petroleum hydrocarbons marine environment pollution is relatively easier detected in the sea bottom sediments than in the highly dynamic water masses. Of course, any pollutant brought by gravitational sinking to the sea bottom — depending on various factors — undergoes destruction or conservation processes. Yet, various pollutants presence in the bottom sediments, impartially of the level of their decomposition, reflects a long-time anthropogenic pressure on the marine environment. This chapter gives a brief overview of the TPHs historical presence in the sediments as well as of investigation results of the Kerch Strait accident impact on the sediments quality.

6.2.1. Historical data

Prior to the Kerch Strait accident on 11 November 2007, sampling of the Kerch Strait bottom sediments for identification of petroleum hydrocarbons presence were carried out on an occasional basis. In November 2003 the maximum concentration of TPHs in the Central part of the Strait exceeded 1090 μg/g (22 PC[1]), while the average was 490 μg/g (see Fig. 6.2.10a). Later expeditions were organized by YugNIRO on 22 October 2005 and, shortly prior to the accident, on 18 October 2007. Their investigation results revealed the presence of the Kerch Strait petroleum pollution ranging from moderate to high levels (Fig. 6.2.1a), (Petrenko O.A., Zhugailo S.S., Avdeeva T.M., 2008). Both studies determined the heavy oil fraction average presence of about 90–170 μg/g, while the TPHs range of presence was recorded as 300–400 μg/g, e. g., 6–8 PC. For both parameters, the maxima were nearly two times higher, e. g., for the heavy oil fractions, the maximum was reaching 400 μg/g on 22 October 2005, and 175 μg/g on 18 October 2007; the TPHs maximal values were correspondingly about 750 μg/g on 22 October 2005 and 500 μg/g on 18 October 2007.

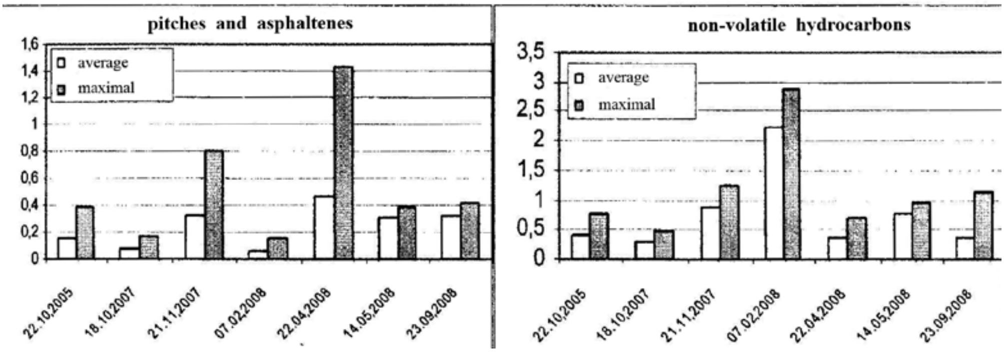

Fig. 6.2.1a. Concentrations variability (mg/g) of pitches and asphaltenes measured by UV-spectrometry (left) and of total petroleum hydrocarbons measured by IR-spectrometry (right) in the Kerch Strait bottom sediments (Petrenko O.A., Zhugailo S.S., Avdeeva T.M., 2008) in the period of October 2005 — September 2008.

Under the Russian monitoring program, on 15 October 2004 a single sample was collected in the port of Caucasus that had TPHs concentration of about 59.5 μg/g (1.2 PC) (Korshenko A. *et al.,* 2009, Korshenko A., 2008). The same sample has revealed the subtotal of polycyclic aromatic hydrocarbons (PAHs) reaching 1011.10 ng/g that slightly exceeded the PC level of 1000 ng/g.

6.2.2. UA: YugNIRO. November 2007 and February, April, May, September, October 2008 and June 2009

Few days after the 11 November 2007 accident, YugNIRO carried out comprehensive studies of petroleum hydrocarbons distribution in the Kerch Strait bottom sediments

[1] Note: In the original Netherlands Lists (Warmer H., van Dokkum, 2002) the Maximum Permissible Concentration (MPC) for mineral oil is 1000 μg/g, whereas the Target Value is 50 μg/g. The latter value was accepted in Russia and Ukraine as Permissible Concentration (PC) in the frame of the routine monitoring system.

(Fig. 6.2.2a). The data made available revealed the maximum of total petroleum hydrocarbons concentration in the bottom sediments reaching very high level of 2024 µg/g of dry weight (equal to 40.5 PC) in the vicinity of the *Volgoneft-139* sunken bow (Fig. 6.2.1a, 6.2.2a). Slightly lower concentration of 1897 µg/g was detected near the *Nahichevan* cargo boat and of 1393 µg/g — at buoy No 27 (to the north of the Temruk Island). Other investigated areas were found less polluted by petroleum hydrocarbons whose levels varied in the range of 493–1000 µg/g reaching the average of about 1250 µg/g (Petrenko O.A., 2008; Zhugailo S.S., 2008; Petrenko O.A., Zhugailo S.S., Avdeeva T.M., 2008; Petrenko O.A. *et al.,* 2008).

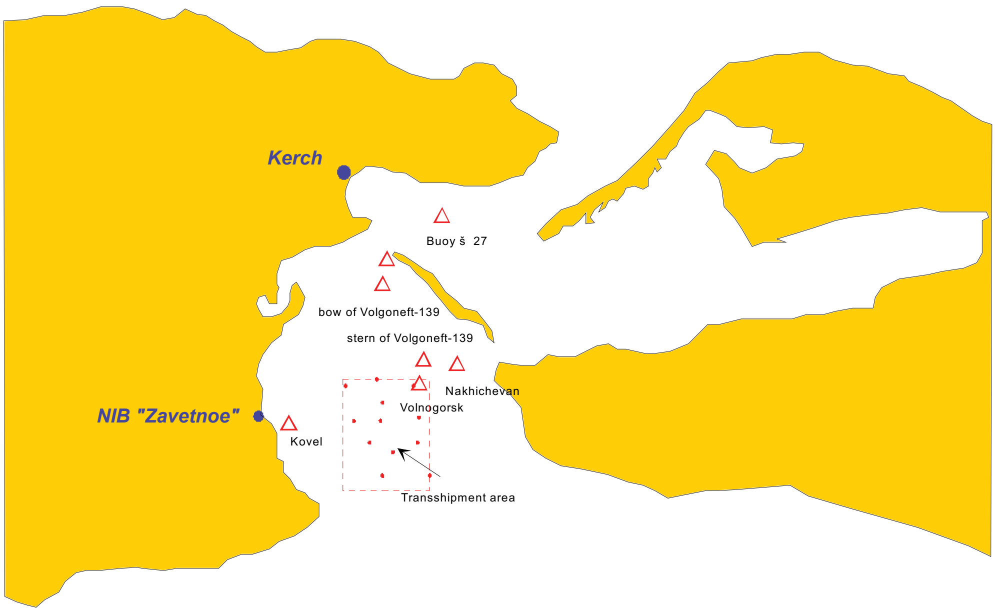

Fig. 6.2.2a. Map of the area investigated by YugNIRO in November 2007 and February 2008.

Less transformed fractions of petroleum hydrocarbons were found dominating in the bottom sediments (61%–93% of the PHs total weight). Strongly transformed fractions of bitumens and asphaltenes were found reaching maximal concentrations of 795 µg/g and 684 µg/g correspondingly near the sunken *Nahichevan* boat and the *Volgoneft-139* bow part.

Further investigations carried out on 7 February 2008 revealed an increase of petroleum hydrocarbons presence near the *Volgoneft-139* grounded stern reaching up to 2988 µg/g and in the vicinity of buoy No 27 — up to 2406 µg/g. Concentrations measured around the *Volgoneft-139* sunken bow were found decreased to 1225 µg/g. The petroleum hydrocarbons heavy fractions share was detected significantly decreased to the level of 2-4% of total weight only. The latter fractions were found mainly concentrated in the Southern part of the transshipment area. In February 2008, the spatial distribution of total petroleum hydrocarbons and oil light fractions was generally uneven in the Kerch Strait demonstrating their decrease from the North to the South. However, the TPHs average level was detected very high reaching about 2250 µg/g.

On 22 April 2008, concentration of bitumens and asphaltenes was found increasing simultaneously with the light fractions decrease due to their washing out from the bottom sediments. TPHs presence averaged around 820 μg/g reaching 1780 μg/g at a single station. The light fractions sediments concentration dropped down two times in the *Volgoneft-139* bow part vicinity and about eight times — by the grounded tanker stern. The maximum heavy fractions concentration was detected in the Northern part of the investigated area, while light oil fractions were dominating in the central parts of the transshipment area.

On 14 May 2008, the TPHs bottom sediments concentration varied in the range of 568–1188 μg/g with the average of about 890 μg/g. Their maximum was detected at the place of the accident and much lower presence was recorded to the South from it.

In the beginning of autumn 2008 (on 23 September), the TPHs maximum was recorded nearly at the same level of about 900 μg/g, nevertheless, the average was about 520 μg/g to reflect a generally decreasing level of the bottom sediments petroleum pollution. Less than a month later the concentration of petroleum hydrocarbons was even lower, but in June 2009 it increased twice and reached 1890 μg/g, obviously unrelated to the Kerch accident.

6.2.3. UA: MHI. December 2007 and March 2008

The TPHs bottom sediments concentration was studied by MHI NASU (Sevastopol) on 6–9 December 2007 and March 2008 (Fig. 6.1.7a). Total petroleum hydrocarbons presence varied in the range of 720–2925 μg/g of dry sediments. The highest reached level of concentration was 58.5 PC (Warmer H., van Dokkum, 2002). The maximum level of pollution was detected at the station located in the Kerch port vicinity and at two sites southwards from the Tuzla Island. The last two spots were very close to the transshipment places area and the *Volgoneft-139* tanker catastrophe. Relatively high levels of TPHs presence were also recorded at the Azov Sea entrance to the Kerch Strait area by stations No 29 and No 37. The results received have clearly indicated a very high level of the bottom sediments petroleum hydrocarbons pollution over the entire Kerch Strait and in the adjacent areas. These data have confirmed the results of previous investigations (Petrenko O.A., 2008; Petrenko O.A. *et al.,* 2008). In some cases the Kerch Strait bottom sediments (fine-grain muddy soft bottom) were found more polluted than sandy bottom sediments located inside the Kerch harbor (Panov B.N., 2006)[2].

6.2.4. UA: IBSS. December 2007 and March 2008

In December 2007 and March 2008, IBSS investigated the Kerch Strait bottom sediments condition at 43 stations in total and at three coastal sites in addition. During the 12–18 December 2007 cruise onboard of the *Experiment* RV, the Kerch Strait sediments samples were collected at 13 stations (Fig. 6.2.4a). Chemical composition of bottom sediments and level of their pollution by petroleum hydrocarbons were determined by applying the chloroform extracting substances (infra-red spectrophotometry). At some stations TPHs water presence was measured as well.

In the major part of the Kerch Strait the bottom sediments were visually muddy having grey or deep-grey color with incorporation of large and small pieces of broken shells of bivalvians, fine and coarse sand. Rather often hydrogen sulphide smell from the samples was felt. At several stations the shells and coarse sand comprised the ma-

[2] The TPHs bottom sediments distribution strongly depends upon those sediments granulometrical condition (size spectrum of particles). Sandy sea bottoms are always less polluted than the fine-grain muddy soft bottoms.

Fig. 6.2.4a. Sampling stations in the Kerch Strait on 12–18 December 2007, IBSS, the *Experiment* RV

jor component of the sediments. The 3–5 mm surface layer of sediments was found oxidized and had a lighter color (Photo).

Photo. A typical sample of bottom sediments from the Kerch Strait, December 2007.

In December, TPHs concentration varied from 3 µg/g to 168 µg/g (3.4 PC) with recorded average of 66 µg/g for 29 treated samples. In March 2008, the sediments contamination level remained the same. In 21 collected samples the TPHs average level was determined as 52 µg/g (1 PC) and variations were less significant ranging between 17 µg/g and 119 µg/g. This level could be considered as a background one for the sediments of those polluted areas with intense shipping traffic. For comparison, the inner part of the Sevastopol Bight had the TPHs sediments presence as high as 6760 µg/g, e. g., about two orders of magnitude higher (Mironov O. G., Kirukhina L. N., Alyomov S. V., 2003).

The IBSS investigation into the bottom sediments carried out soon after the Kerch catastrophe indicated absence of significant petroleum pollution resulting from the oil spill. In general, the recorded level was typical for those chronically polluted areas of the Azov and Black Seas. However, this investigation outcome contradicted the other institutions results indicating significant increase of bottom sediments pollution by TPHs after the oil spill accident in November 2007 (see Summary).

6.2.5. RU: The Shirshov IO RAS. February-March, July 2008

On 28 February-9 March 2008, the Shirshov Institute of Oceanology (SIO of the Russian Academy of Sciences) and WWF undertook a joint field trip along the Taman coast (Spiridonov V.A. *et al.,* 2008). The trip main tasks were as follows: to visually assess oil pollution of the coast; to determine contamination level of the coastal waters bottom sediments; to determine the biota oil contamination (of the bottom-dwelling organisms); to assess biological diversity of benthic communities present in the typical marine habitats for monitoring of potential changes and determining the benthic (bivalves) physiological state in order to assess the oil impact on them.

The exploration survey covered the Chushka and Tuzla Spits coasts and the shore line between the Ilyich and Cuchuguru villages, as well as the Dinsky and Taman Bays coasts. In the coastal zone, 39 divings and samplings were carried out (Fig. 6.2.5a). In total, 35 samples of bottom sediments, 66 samples of macrozoobenthos, 33 samples of visually contaminated aquatic organisms, to include 26 samples of animals and 7 samples of plants, and 8 samples of shellfish (for physiological state analysis) were collected. In addition, 15 descriptions of bottom vegetation were completed.

Fig. 6.2.5a. Scheme of the sea bottom visual diving survey and samples collection at the Kerch Strait Russian coast, 28 February — 9 March 2008 (Spiridonov V.A. *et al.,* 2008; Koluchkina G.A., 2009).

Concentration of aliphatic hydrocarbons in the bottom sediments was measured (the Shimadzu GC-2010 high resolution gas chromatograph) at 35 stations within the Kerch Strait, Taman and Dinsky Bays coastal zones. The aliphatic hydrocarbons concentration varied spatially within the range of 0.01–1.77 μg/g. All results of research into aliphatic substances were recalculated into total petroleum hydrocarbons and presented in Figure 6.2.5b. Their maximum value of 1106 μg/g was registered at the Dinsky Bay station located 300 m offshore (to the South-West from the Chushka Spit at a distance of about 6 km from the Ilyich village). In those shallow waters (0.4 m deep) overgrown with reed, the sediments were either a slimy bottom or fine-grain pelitic sand with a high level of fine fractions (Fig.6.2.5c, St. 3,4,5a,5b in the Dinsky Bay). In addition to high percentage of 0.05 mm and less diameter fine fractions that varied from 9.15 % to 14.77 %, a rather high concentration of 3.28 % of organic matter was recorded at the same spot as well. Similar slimy bottom areas were also found in the Dinsky Bay Northern part (St. 14,15,16), close to the Chushka Spit Southern end (from the Dinsky Bay side, St. 33, 0.4 m deep) and in the Taman Bay (few km away from the Sennoi village, St. 35a, 35b, 3.5–4.0 m deep). High concentration of hydrocarbons was recorded there reaching 113–250 µg/g, 311 µg/g and 729–888 µg/g respectively, and it was associated with strong presence of organic matter and high percentage of fine fractions in the bottom sediments as well. At all the above mentioned sites, slimy sand consisted of pelitic particles.

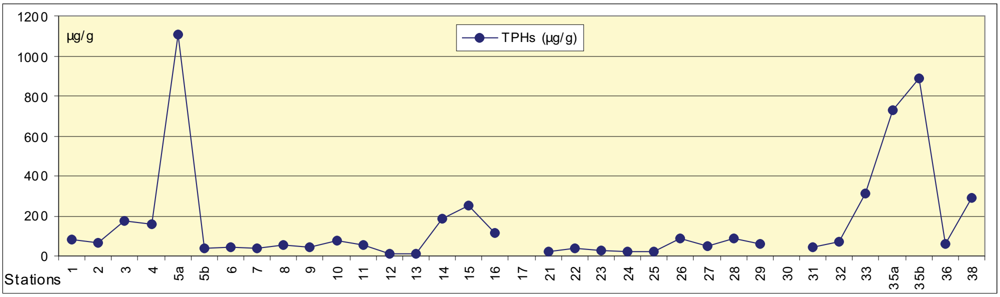

Fig. 6.2.5b. Concentration of petroleum hydrocarbons at the stations located in the shallow waters in the Kerch Strait, Dinsky and Taman Bays during the period of 28 February — 9 March 2008 (Spiridonov V.A., *et al.*, 2008).

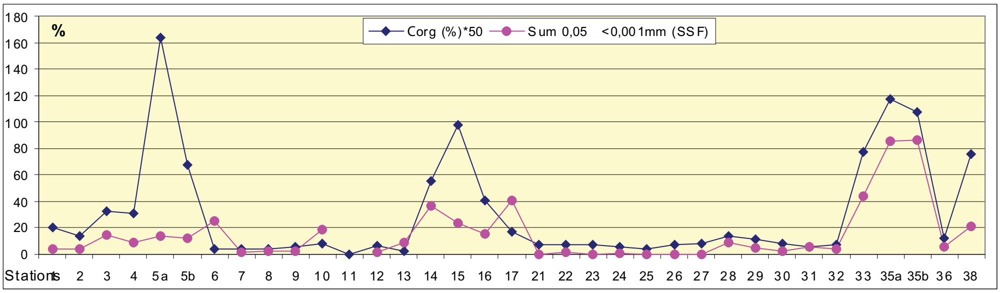

Fig. 6.2.5c. Percentage of organic matter (multiply 50) and small-size fractions (SSF) of 0.05 mm and less diameter in the bottom sediments of the Kerch Strait, Dinsky and Taman Bays during the period of 28 February — 9 March 2008 (Spiridonov V.A. *et al.*, 2008).

Concentration of petroleum hydrocarbons on the surface of small-size particles is largely associated with increase in their presence in the sediments with high share of organic matter and/or fine fractions of pelitic origin. To reduce it, normalization method is traditionally applied[3]. After normalization, the hydrocarbons still relative abundance would point out to the places of abnormal pollution in comparison to the areas with background ratio of organic matter and hydrocarbons to potentially reflect the aftermath of the oil spill accident.

[3] TPHs/Corg ratio is calculated. Corg — concentration of organic matter.

Few sites were determined at the Kerch Strait having the TPHs/Corg ratio higher than the background ratio of 294 (average calculated for this set of data, as historical data are absent for the area), (Fig. 6.2.5d). The maximum was recorded in the Chushka Spit coastal area between the Ilyich village and the Ahilleon Cape that were heavily polluted during the oil spill accident in November 2007. That location was not specified either in terms of high natural hydrocarbons concentration[4], or organic and small fractions presence in the sediments. Hence, an increased TPHs/Corg ratio revealed the presence of the spill residual effect. Other places with increased ratio were found close to the Taman city (St. 26) and at the Chushka Spit Southern end (from the Kerch Strait side). Also, both sites were affected during the Kerch accident.

The TPHs and smaller size fractions (SSF) ratio did not follow the TPHs/Corg one. It mainly had values close to zero. Only few stations reflected certain elevation of the parameter: In the coastal zone of central and Northern parts of the Tuzla Spit from the Taman Bay side (St. 23, 25); in the coastal waters nearby the Taman town (St. 26) and the highest ratio of 2550 was detected at the Northern coast of the Chushka Spit from the Kerch Strait side (St. 27). The last area was one of the most polluted during the November 2007 oil spill accident.

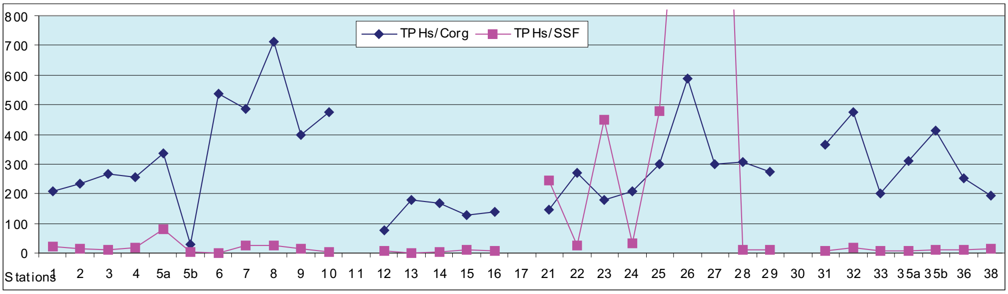

Fig. 6.2.5d. Concentration of total petroleum hydrocarbons normalized, in percentage to organic matter and fine fractions of 0.05 mm and less diameter, present in the bottom sediments in the Kerch Strait, the Dinsky and Taman Bays in the period of 28 February-9 March 2008 (Spiridonov V.A., *et al.*, 2008).

The next expedition of SIO RAS was carried out on 16–31 July 2008. Sampling was organized along the coasts of the Chushka Spit and Tuzla Island, and in the Dinsky and Taman Bays (39 stations, Fig. 6.2.5e). Coastal visual surveys were conducted at 18 stations and the bottom of the Strait was surveyed at 21 stations to collect 36 bottom sediments samples for further analysis for aliphatic hydrocarbons presence (Gas-Liquid chromatography — GC).

Practically no visual traces of heavy fuel oil presence in the water area were detected. The total organic carbon concentration in the bottom sediments varied from 0.02 % to 5 %, while the aliphatic hydrocarbons concentration fluctuated from 0.03 µg/g at the Tuzla sand beach to 17.3 µg/g in the inner part of the Dinsky Bay. The mean hydrocarbons concentration was considerably high reaching 2.45 µg/g. However, the bottom sediments detailed analysis revealed at majority of examined sites the presence of pollution that had undergone intensive processes of biodegradation and resedimentation. Hence, it could not be concluded that the Kerch Strait oil spill was the only source of

[4] A naturally high level of hydrocarbons recorded in the bottom sediments of the Kerch Strait, Taman and Dinsky Bays shallow waters could be related to high level of biological activity of the reeds, macrophytes and plankton communities present there.

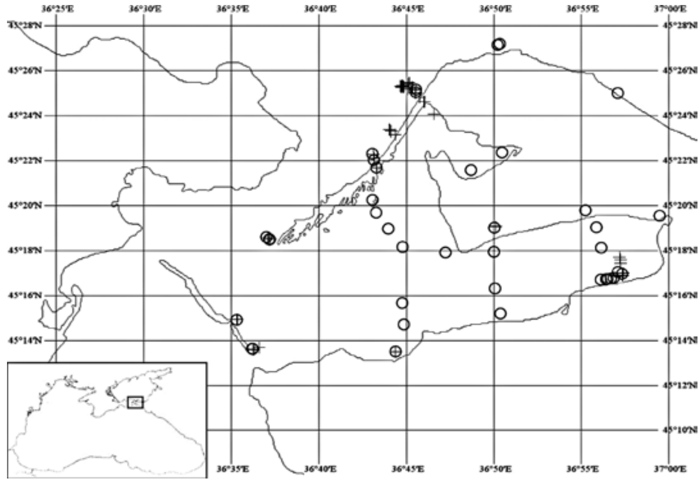

Fig. 6.2.5e. Scheme of observation stations operational during the SIO RAS expedition on 16–31 July 2008 (Koluchkina G.A., 2009). The stations operational during the first expedition on 28 February-9 March 2008 are marked with crosses.

pollution detected. The available data was insufficient for distinguishing the heavy oil spill hydrocarbons discharged during the Kerch accident from the region's chronic anthropogenic pollutants.

6.2.6. UNEP Expedition: July 2008

UNEP carried out its expedition to the Kerch Strait in Ukraine's littoral and costal zones during the period of 15–25 July, 2008 (Fig. 6.2.6a). Six bottom sediments samples were collected at the fairway of the Kerch-Enikale channel in the vicinity of the Tuzla Island

Fig. 6.2.6a. Stations location scheme. UNEP expedition to the Kerch Strait of 15–25 July, 2008 (UNEP, 2008, http://www.sea.gov.ua).

at the depth of 2–8 m, while another 12 samples of sand with grass were collected at the beaches stretching from the Cazantip Cape to the Zavetnoe village in the Southern part of the Kerch Strait. Heavy fractions of petroleum hydrocarbons, i. e. naphthenes (cycloalkanes) and paraffins (alkane hydrocarbons), were determined as dominating and reaching the 80–90% levels in all samples (Fig. 6.2.6b). Concentration of those substances was 42–110 μg/g of dry soil in the samples collected in the littoral areas (Stations No 18–25). Their sediments presence was going up to 300–600 μg/g closer to the *Volgoneft-139* tanker sunken bow part. No visual traces of heavy fuel oil were detected at the bottom of the area surveyed (UNEP, 2008).

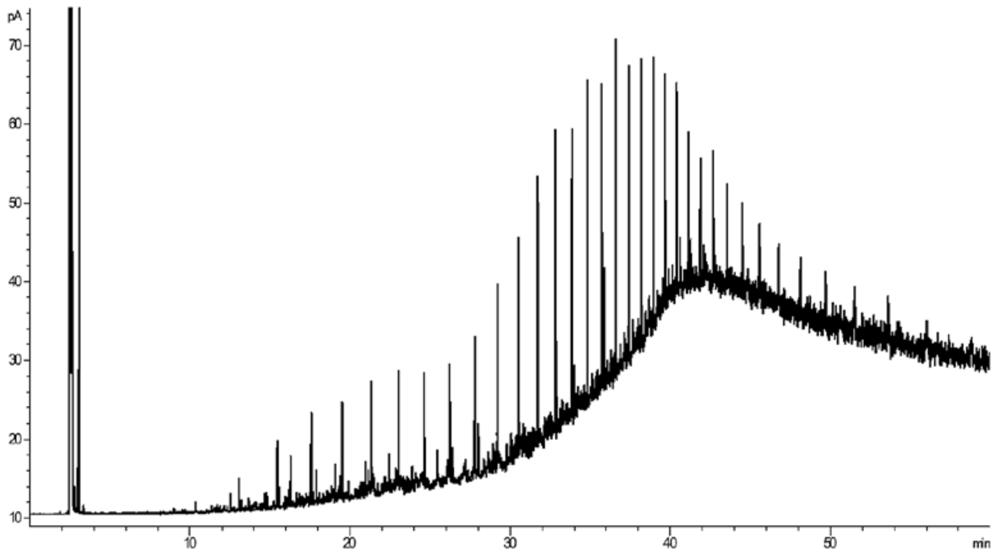

Fig. 6.2.6b. Chromatogram of M-100 oil transported by the *Volgoneft-139* tanker. Domination of heavy oil fractions (C10-C35) is obvious. (UNEP, 2008, http://www.sea.gov.ua).

6.2.7. RU: ChAD. July, August, November and December 2008

At 154 stations, TPHs presence in the bottom sediments upper layer was studied during three seasons of 2008 (Fig. 5.2.1a). In all collected samples the average concentration was reaching 20.8±36.7 μg/g, while several samples were discovered having TPHs concentration below the detection limit, e. g. analytical zero. The maximum concentration measured stood at 184.6 μg/g that was equal to 3.7 permissible concentrations (PC) for bottom sediments in accordance with the Netherlands Lists (Warmer H., van Dokkum, 2002). Well expressed patchiness of TPHs distribution in the bottom sediments was also recorded (Fig. 6.2.7a-c).

In summer 2008, three rather small areas with concentrations exceeding 1 PC were determined near the port of Caucasus at the Chushka Spit at the South-West from the Crimean coast and southward of the Tuzla Island. Slight increase in presence as compared with background concentrations was recorded in the area southward of the Enikale Cape. Patches of higher TPHs concentration detected could have originated from the Kerch Strait accident. The most polluted spots at the bottom were found by the Tuzla Island between the Chushka Spit and the Crimean Peninsula coast to the South from the Enikale Cape, and by the Western part of the Taman Peninsula between the Panagia Cape and Tuzla Cape also.

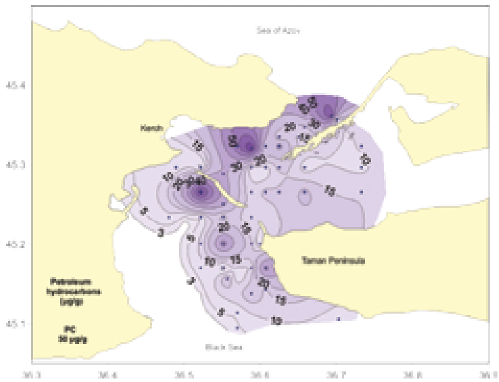

Fig. 6.2.7a. Petroleum hydrocarbons concentration (µg/g) in the Kerch Strait area bottom sediments averaged for July and August 2008.

In November 2008, only one patch with high concentration level (exceeding 50 µg/g up to 139.2 µg/g) was found. Its location was different from the sites inspected in summer being to the South from the Chushka Spit within the Taman Gulf (Fig. 6.2.7b). The second maximum observed in the Kerch Strait by the Chushka Spit was 30.8 µg/g. The rest of investigated areas had a very low hydrocarbons concentration usually standing at below 5 µg/g. The place where the *Volgoneft-139* tanker bow part sank had the cleanest bottom sediments as compared to all the other areas investigated.

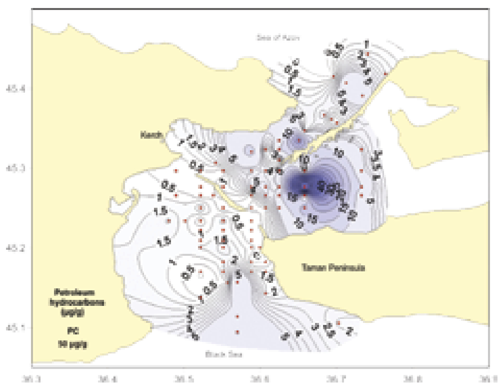

Fig. 6.2.7b. Petroleum hydrocarbons concentration (µg/g) in the Kerch Strait area bottom sediments in November 2008.

Strangely enough, a significant increase in TPHs concentration was observed in December 2008 as compared with November (Fig. 6.2.7c). Large sections of the investigated area (44 % of stations) appeared to contain the bottom sediments polluted by petroleum hydrocarbons above the norm of 50 µg/g (Warmer H., van Dokkum R., 2002). Variation was high to range within 2.7–184.6 µg/g and the recorded maximum was 3.7 PC. Several stations with maximal TPHs presence were located to the South of the Tuzla Island and close to the *Volgoneft-139* place of accident. Meanwhile, almost all the sampled stations to the North of the Tuzla Island, including those in the Taman Bay, were also found to have a very high TPHs concentration level. Such a significant difference in petroleum hydrocarbons concentration data obtained in the result of two consecutive surveys (November, December) may imply that sources of pollution other than the oil spill accident of November 2007 were present, or that some kind of a serious analytical mistake was made in application of investigation methodology in November. Actually, the data collected in November evidenced an extremely low concentration that has made the results look quite doubtful.

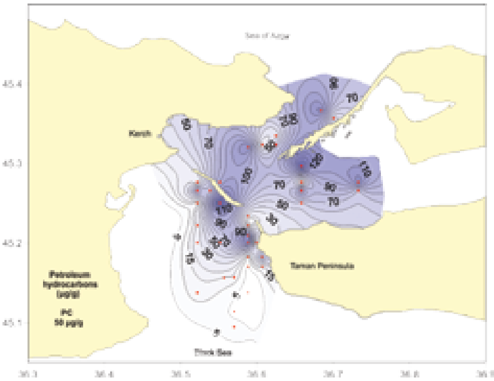

Fig. 6.2.7c. Petroleum hydrocarbons concentration (µg/g) in the Kerch Strait area bottom sediments in December 2008.

6.2.8. UA: UkrSCES. July 2009 (30th cruise of the Vladymyr Parshin RV)

During the 30th cruise of the *Vladymyr Parshin* RV on 8 July 2009, samples of the Kerch Strait bottom sediments were collected at 12 stations (see Chapter 5, Fig. 5.2.1a). Concentration of total petroleum hydrocarbons was investigated by means of an infra-red spectrophotometer with the Simard standard (Manual, 1996), while the level of total aromatic hydrocarbons (TAHs) was measured by means of spectrofluorometer with Ropme standard (Methods, 1992). Also, the same samples were studied for determining the concentration of organic carbon and phenols (Methods, 1995), (Tab. 6.2.8a).

Table 6.2.8a. Average concentration of total petroleum hydrocarbons, total aromatic hydrocarbons and phenols (µg/g), and organic carbon (%) in the Kerch Strait bottom sediments on 8 July 2009.

Parameters	Organic C, %	Phenols, µg/g	TAHs, µg/g	TPHs, µg/g
Average	0.900	0.78	15.8	149
Minimum	0.080	0.48	3.43	70
Maximum	2.076	1.35	23.3	265

TPHs and TAHs average concentration in the Kerch Strait waters exceeded the norm by about 3 times (Fig. 6.2.8a). Such a high level of TAHs could be attributed to the consequences of the Kerch Strait accident. Generally, aromatic hydrocarbons have a high molecular weight typical for heavy fuel and they may remain relatively resistant to chemical and microbial degradation for protracted periods of time.

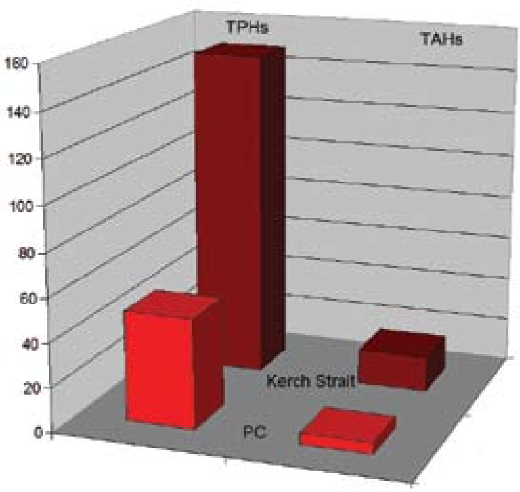

Fig. 6.2.8a. Average concentration of TPHs and TAHs (µg/g) in the Kerch Strait bottom sediments on 8 July 2009.

As for the TPHs spatial distribution, a patch of high concentration was detected in the Crimean coastal zone westward from the Tuzla Island (Fig. 6.2.8b).

Fig. 6.2.8b. Real and aluminum normalized TPHs distribution in the Kerch Strait bottom sediments on 8 July 2009.

Strong interdependence existing between the bottom sediments granulometric structure and concentration of organic compounds including petroleum hydrocarbons is well known and it has been already mentioned above. Small clay and silt fractions have a strong capacity to keep pollutants attached to the surface of their particles (a good adsorbent of pollutants). Aluminum concentration is used for measuring the clay particles share of presence in the sediments and in the TPHs normalization process. The normalized distribution of petroleum hydrocarbons (TPHs/Al) has clearly shown that the bottom sediments maximum pollution occurred in the place of the Kerch Strait accident. However, one year and a half after the Kerch accident it is unlikely to still have the consequences of the Kerch oil spill itself only observed in the sediments. Most probably the elevated level of sediments pollution in this particular location is chronic and related to the nearness of the Kerch Strait transshipment area to the studied site.

Polycyclic Aromatic Hydrocarbons. The polycyclic aromatic hydrocarbons highest concentration in the bottom sediments was mainly detected by the Crimean cost slightly to the South from the Kerch Bight. PAHs average concentration exceeded PC by 3–5 times according Netherlands Lists (Warmer H., van Dokkum, 2002), (Tab. 6.2.8b and Fig. 6.2.8c).

Table 6.2.8b. Statistical characteristics of individual PAHs (ng/g) present in the Kerch Strait bottom sediments on 8 July 2009.

Parameters	Average	Minimum	Maximum	PC
Naphtalene	34.0	4.4	103	15
Acenaphthylene	5.0	2.1	10.8	
Acenaphthene	4.8	1.1	7.0	
Fluorene	45.0	18.7	67.3	
Phenanthrene	229	149	330	45
Anthracene	7.3	1.9	15.5	50
Fluoranthene	122	23.8	302	15
Pyrene	75.0	9.6	182	
Benzo(a)anthracene	45.0	3.7	136	20
Chrysene	61.0	8.0	186	20
Benzo(b)fluoranthene	77.0	13.0	158	
Benzo(k)fluoranthene	84.0	16.0	218	25
Benzo(a)pyrene	46.0	3.7	115	25
Indeno(1,2,3cd)pyrene	49.0	12.5	95.6	25
Dibenzo(a, h)anthracene	10.0	1.1	25.0	
Benzo(g,h,i)perylene	51.0	10.5	101	20

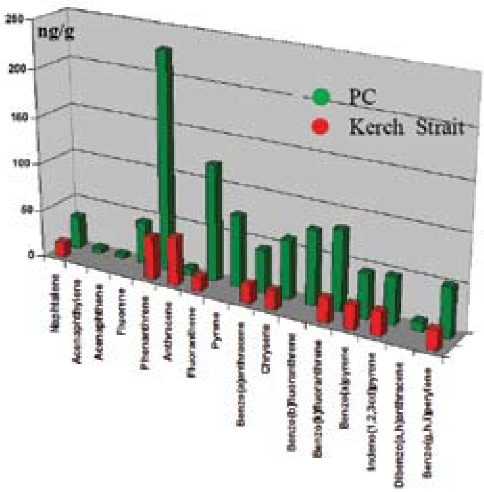

Fig. 6.2.8c. Average concentration of individual PAHs in the Kerch Strait bottom sediments on 8 July 2009.

6.2.9. UA: UkrSCES. December 2009 (31st cruise of the Vladymyr Parshin *RV)*

On 4–15 December 2009, the Ukrainian Scientific Center of Ecology of the Sea (Odessa) carried out a second detailed research into the Kerch Strait bottom sediments petroleum hydrocarbons pollution onboard of the *Vladymyr Parshin* RV (31st cruise), (Fig. 5.2.5.2a, Fig. 5.2.5.2b). As a result, 32 samples were collected. In general, levels of petroleum pollution and phenols concentration were exceeding the norms almost in all the bottom sediments studied (Tab. 6.2.9a, Fig. 6.2.9a.).

Table 6.2.9a. Statistical characteristics of TPHs, TAHs, phenols and organic carbon present in the Kerch Strait bottom sediments in December 2009.

Parameters	Average	Median	Minimum	Maximum	Standard deviation
TPHs, µg/g	102.6	100	60	140	23.1
TAHs, µg/g	11.41	5.36	1.83	44.40	12.80
phenols, µg/g	0.76	0.68	0.45	1.15	0.233
organic C, %	0.927	0.77	0.08	3.32	0.818

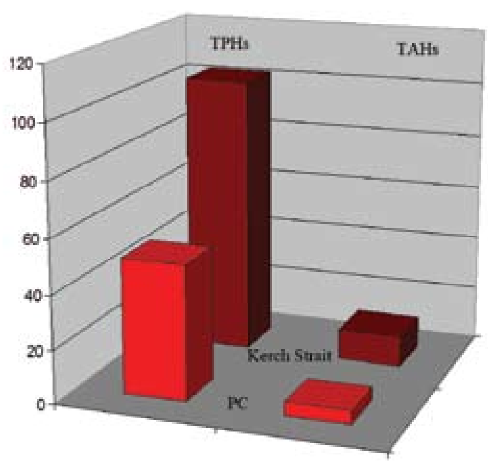

Fig. 6.2.9a. Average concentrations of TPHs and TAHs (µg/g) present in the Kerch Strait bottom sediments in December 2009.

The normalized distribution of petroleum hydrocarbons (TPHs/Al) has revealed the spots of petroleum hydrocarbons maximal concentration by the *Volgoneft-139* tanker sinking place in November 2007 (and transshipment area at the same time) and slightly northward from it in the proximity of the Tuzla Island Western end (Fig. 6.2.9b).

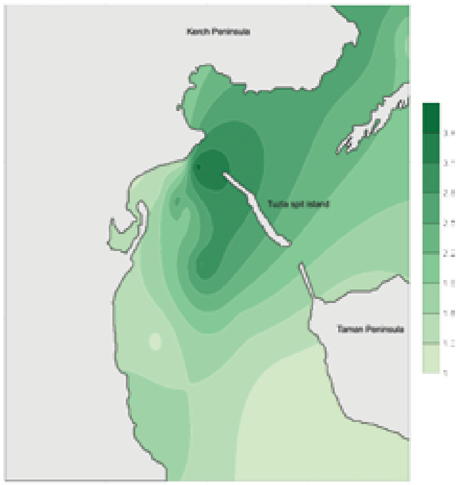

Fig. 6.2.9b. Spatial distribution of Aluminum normalized petroleum hydrocarbons in the Kerch Strait bottom sediments in December 2009.

The chronic character of the Kerch Strait sediments petroleum pollution was confirmed by a high concentration of polycyclic aromatic hydrocarbons (Table 6.2.9b).

Table 6.2.9b. Statistical characteristics of individual PAHs (ng/g) present in the Kerch Strait bottom sediments in December 2009.

Parameters	Average	Median	Minimum	Maximum	Standard deviation
Naphtalene	39.10	39.8	10.9	70.3	14.98
Acenaphthylene	2.913	2.63	1.23	5.74	1.320
Acenaphthene	7.265	6.85	2.0	13.10	2.572
Fluorene	27.34	23.8	13.1	60.3	12.93
Phenanthrene	84.62	83.4	40.4	142.0	23.82
Anthracene	26.85	26.1	10.7	52.6	11.51
Fluoranthene	51.80	43.2	20.1	109.0	27.77
Pyrene	44.0	40.2	15.9	90.8	21.99
Benzo(a)anthracene	56.93	53.1	8.4	106.0	29.37
Chrysene	56.86	60.1	6.9	121.0	28.50
Benzo(b)fluoranthene	49.42	40.2	10.3	151.0	33.08
Benzo(k)fluoranthene	43.96	33.7	12.3	99.5	24.91
Benzo(a)pyrene	28.63	24.4	5.7	95.6	18.25
Indeno(1,2,3cd)pyrene	25.60	24.6	4.3	78.0	15.94
Dibenzo(a,h)anthracene	8.65	6.4	1.2	40.1	7.54
Benzo(g,h,i)perylene	25.10	22.6	3.4	51.4	12.60

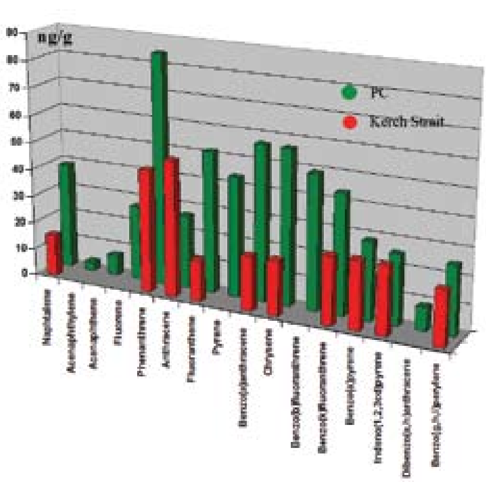

Fig. 6.2.9c. Average concentration of individual PAHs in the Kerch Strait bottom sediments in December 2009.

Among the 16 studied individual PAHs, phenanthrene, fluoranthene, naphthalene, pyrene, benzoanthracene, benzofluoranthene and benzo(a)pyrene revealed the highest level of presence (Fig. 6.2.9c). All these chemical substances are highly toxic and may remain stable in marine environment without chemical or microbiological degradation for protracted period of time.

As compared with July, the TPHs and TAHs presence decreased in December by 1.4 times or 30% (Fig. 6.2.9d), however the TPHs and PAHs concentrations ratio remained unchanged.

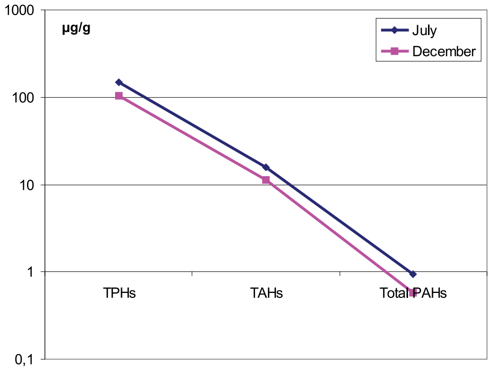

Fig. 6.2.9d. Concentration of petroleum hydrocarbons (µg/g) in the Kerch Strait bottom sediments in July and December 2009.

Quality control, concurrent measurements. Different laboratories in the Black Sea area measure the level of such priority pollutants as various forms of hydrocarbons, pesticides, PCBs and trace metals as shown in this book. To verify the comparability of those measurement results, an interesting inter-calibration exercise was undertaken during the December 2009 cruise of the *Vladymyr Parshin* RV. One and the same person applying the same equipment was taking identical portions of sediments from one and the same grab at ten stations for their further parallel analysis to be carried out by analytical laboratories of UkrSCES (Odessa, Ukraine) and the Typhoon Chemical-Analytical Center (Obninsk, Russian Federation). Stations for shared bottom sediment analysis were mainly placed in the inner part of the Kerch Strait (marked in red in Fig. 6.2.9e).

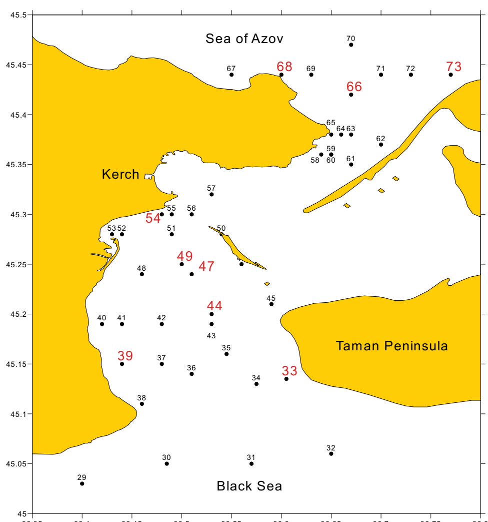

Fig. 6.2.9e. Stations for bottom sediments sampling installed at the Kerch Strait during the 31st cruise of the *Vladymyr Parshin* RV for the period of 4–15 December 2009. The duplicated stations are marked in red.

Sampling of the Kerch Strait bottom sediments during the 31st cruise of the *Vladymyr Parshin* RV was basically carried out in the rough weather conditions close to stormy.

A Van-Veen grab with electric-powered winch was used for those samplings. After its uplifting, the grab was placed on the vessel deck. Subsampling was conducted by a chemist by means of a stainless steel scoop. With its help and by identical manipulations four portions were taken from one and the same spot of the sediments surface in the grab. Two of them meant for the trace metals analysis were put into the plastic bags, while the second pair meant for organics analysis got covered by aluminum foil before being put into the plastic bags. All subsamples were collected from the upper layer of the bottom sediments. Immediately after that, the bags with subsamples were placed into a fridge with a temperature regime of minus 18^0C. Half of those duplicated subsamples were treated in Odessa, Ukraine (UkrSCES), while another half — in Obninsk, the Russian Federation (Typhoon) as mentioned above.

Based upon the results received, it became possible to identify a methodological error made during the procedure of subsampling from the grab. A common suggestion would be that both chemical laboratories in Odessa and Obninsk were highly professional in carrying out the analysis of all chemical parameters under study. The statement is based not only on the fact of both laboratories having modern sophisticated equipment, trained personnel and well developed QA/QC procedures, but on the basis of their regular participation in different intercalibration exercises and excellent results achieved as well (like QUASIMEME, IAEA, etc.). For instance, the high level of professionalism possessed by both laboratories allowed to choose them as reference units for the bottom sediments chemical analysis within the recent TACIS Caspian Sea Project entitled the «Caspian Water Quality Monitoring and Action Plan for Areas of Pollution Concern» (Voitsekhovitch O., 2009). However, the intercalibration exercise described here showed substantial differences in the results of the two laboratories for some parameters.

As the granulometry analyses done by both laboratories have shown, sediments in the Southern part of the Kerch Strait are rather rough and have a low presence of small fractions, while the sediments of the central and Northern parts of the Strait have an increased clay fraction presence (Fig.6.2.9f). In general, the difference in the two laboratories results varied within the range of 2.7–22.4 % with the exception of Station No47 revealing a 52.5 % difference. There were two options to explain such a big difference — either an analytical error was made or a non-equal subsampling from the grab was carried out. The latter option was found more probable, having in mind the professionalism of the laboratories involved.

Both laboratories reported similar total organic carbon (TOC) concentration levels for the bottom sediments (Fig. 6.2.9g). Their recorded difference varied from a very low level of 0.26 mg/g to l11.84 mg/g, while no principle disagreement was observed. In this connection, it is recommendable to normalize the pollutants concentration on organic carbon content.

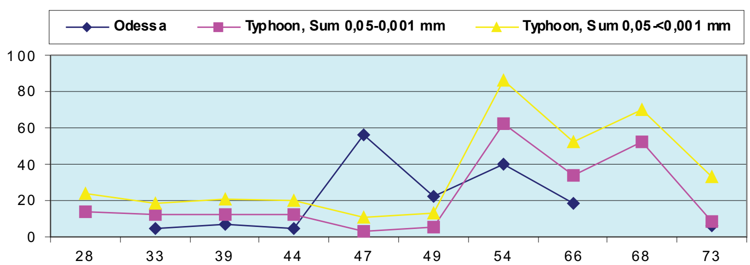

Fig. 6.2.9f. Percentage of small fractions present in the Kerch Strait bottom sediments as measured in parallel by UkrSCES (Odessa) and Typhoon (Obninsk) on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

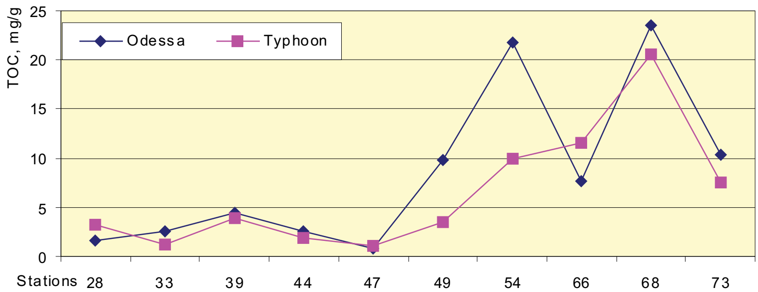

Fig. 6.2.9g. Concentrations of total organic carbon (TOC, mg/g) in the Kerch Strait bottom sediments simultaneously measured by UkrSCES (Odessa) and Typhoon (Obninsk) on 8–11 December 2009, 31st cruise of the «*Vladymyr Parshin*» RV.

PAHs. The data provided by Odessa and Obninsk on the individual polycyclic aromatic hydrocarbons concentration subtotal significantly differed (Fig. 6.2.9h). Mean concentration of the whole first set of subsamples (Odessa) stood at 655 µg/g, while the second set (Obninsk) averaged 4.3 times lower standing at 153 µg/g. Approximately the same ratio was recorded for individual polyaromatic substances, for instance, the benzo (a) pyrene concentration in Odessa subsamples averaged 31.3 µg/g and in the Obninsk set — 10.6 µg/g.

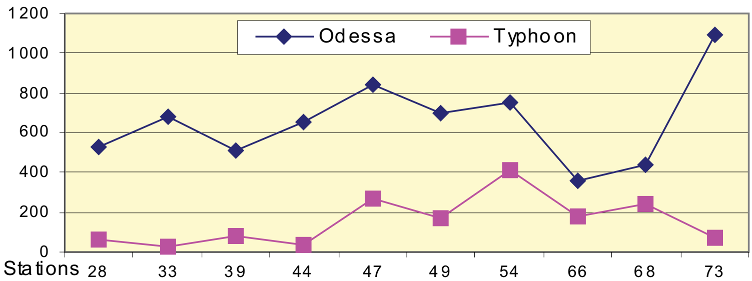

Fig. 6.2.9h. Concentration of total polycyclic aromatic hydrocarbons (PAHs, µg/g) in the Kerch Strait bottom sediments on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

At the same time, the PAHs/TOC ratio obtained by both laboratories revealed a similar spatial distribution with a visible maximum present in the place of the *Volgoneft-139* shipwreck (Fig. 6.2.9i).

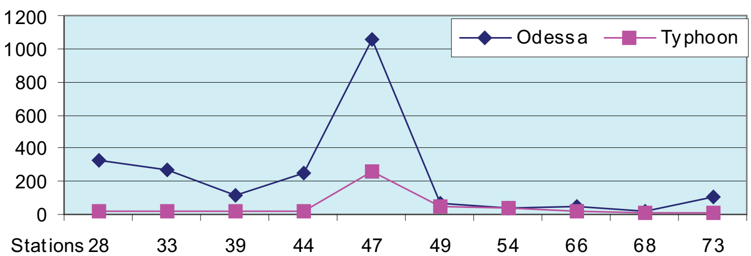

Fig. 6.2.9i. Normalized concentration of total polycyclic aromatic hydrocarbons (PAHs, µg/g) on organic carbon content (C_{org}, mg/g) in the Kerch Strait bottom sediments on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

Similar exercises to normalize aromatic substances concentration in percentage to small fraction of the bottom sediments were performed by both laboratories (Fig.

6.2.9j). The data made available by the Typhoon subsamples have clearly indicated only one maximum detected close to the shipwreck. Results received from Odessa did not allow the same conclusion.

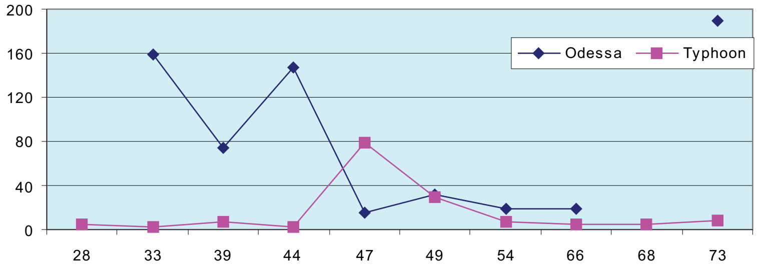

Fig. 6.2.9j. Normalized concentration of total polycyclic aromatic hydrocarbons (PAHs, µg/g) on concentration of small particles (%) in the Kerch Strait bottom sediments on 8–11 December 2009 during 31st cruise of the *Vladymyr Parshin* RV.

The working hypothesis of an increased polycyclic aromatic hydrocarbons concentration in the Kerch accident place was tested additionally through applying the Aluminum normalization concentration (the fine clay fractions indicator in the soil). Both laboratories recorded a peak at Station No 47 and an additional one in each set of data (Fig. 6.2.9k).

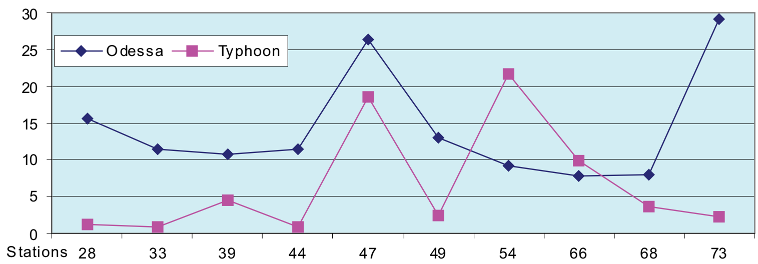

Fig. 6.2.9k. Normalized concentration of total polycyclic aromatic hydrocarbons (PAHs, µg/g) on Aluminum concentration (mg/g) in the Kerch Strait bottom sediments on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

Evaluation of three different types of aromatic hydrocarbons normalization made it possible to conclude that a clear relation existed between the PAHs and total organic carbon concentrations. The PAHs/TOC ratio made it possible to determine the place of the *Volgoneft-139* shipwreck though two years had already passed since the Kerch catastrophe. However, as mentioned above, the latter might be well related to chronic pollution and nearness of the transshipment area.

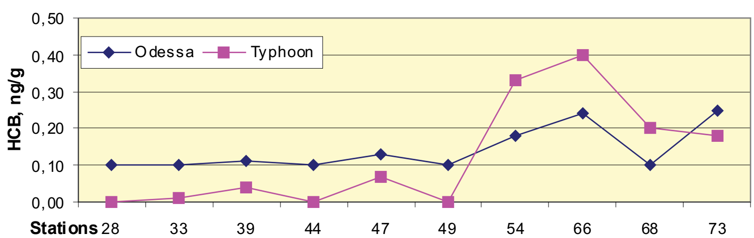

Fig. 6.2.9l. Concentration of HCB (ng/g) in the the Kerch Strait bottom sediments on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

Pesticides. Analyses of chlorinated pesticides concentration in the Kerch Strait bottom sediments could be considered as non-satisfactory due to a revealed large difference in data sets provided by the two laboratories. The mean values received — 0.14 ng/g by Odessa and 0.12 ng/g by Obninsk — were very close (Fig. 6.2.9l). However, the metabolites subtotal of HCHs (2.67 and 0.07 ng/g respectively) and DDTs (3.13 and 0.17 ng/g respectively) differed significantly by 1 or 2 orders of magnitude.

Metals. Among the tested metals of Al, Fe, As, Cd, Cr, Cu, Pb, Mn, Hg, Ni and Zn, some parallel sets like for chromium (means of Odessa versus Typhoon were 55.9 µg/g/39.3 µg/g), zinc (52.17 µg/g/40.86 µg/g) and cooper (13.1 µg/g/11.7 µg/g) had rather more similarity than difference, and the errors made by the laboratories could be considered as small (Fig. 6.2.9m, Fig. 6.2.9n).

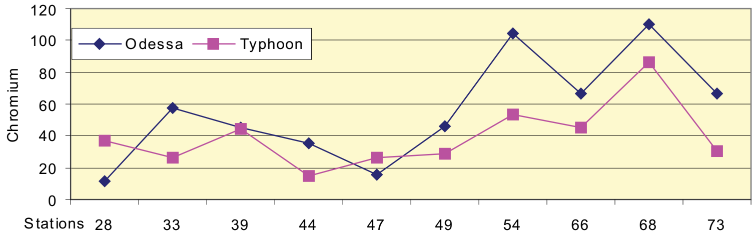

Fig. 6.2.9m. Concentration of chromium (µg/g) in the Kerch Strait bottom sediments on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

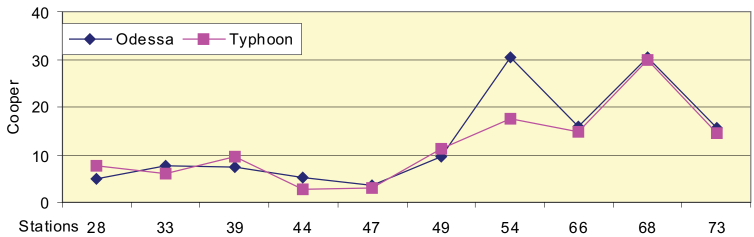

Fig. 6.2.9n. Concentration of cooper (µg/g) in the Kerch Strait bottom sediments on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

Quality results were obtained for aluminum (50 240 µg/g/53 245 µg/g), nickel (24.8 µg/g/22.6 µg/g) and mercury (0.030 µg/g/0.022 µg/g), (Fig. 6.2.9o).

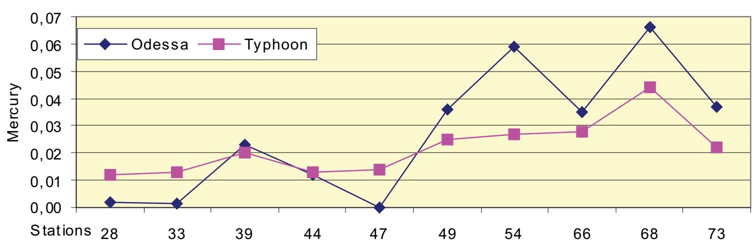

Fig. 6.2.9o. Concentration of mercury (µg/g) in the Kerch Strait bottom sediments on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

Worse results were obtained for lead, and every sample from Odessa had a significantly higher concentration than the one from Typhoon. As a result, the means differed substantially, i. e., 14.8 µg/g and 5.04 µg/g respectively (Fig. 6.2.9p).

Conclusions. Concurrent measurement of important chemical parameters of similar subsamples from one and the same grab, and their further treatment by highly experienced laboratories having sophisticated equipment and well-trained personnel have revealed

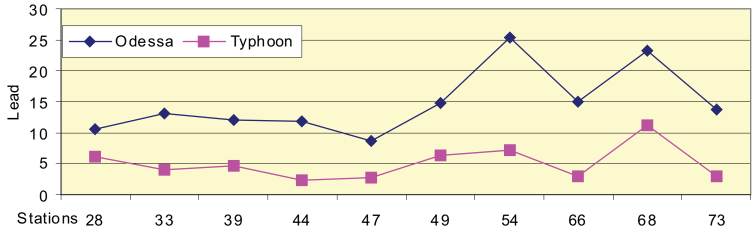

Fig. 6.2.9p. Concentration of lead (µg/g) in the Kerch Strait bottom sediments on 8–11 December 2009, 31st cruise of the *Vladymyr Parshin* RV.

a significant difference in the results obtained. The two participating laboratories reported similar data results of TOC and some metals. Few parameters like copper have showed high data similarity. The organic pollutants data — PCBs and Pesticides — differed by 2–3 orders of magnitude. Disparity in results could be attributed to a methodological error made in the process of subsampling from the grab but, probably, also to the sampling preparation and analytical procedures further applied. Therefore, it is recommended to pay special attention to the quality control measures already at the sampling and subsampling stages. The extent of potential divergence of data obtained in different cruises and by different laboratories is easy to imagine, when such a huge difference is revealed in the result of a parallel subsamples analysis from one and the same grab.

6.2.10. Summary: Bottom Sediments Pollution by TPHs

The temporal dynamics of TPHs concentration in the Kerch Strait bottom sediments has clearly reflected the impact of the November 2007 oil spill accident. Rapid and significant increase of TPHs presence in the sediments was evidenced by various data received in different expeditions (Fig. 6.2.10a). Two institutions, YugNIRO and MHI registered high TPHs presence to exceed the norm by almost 60 times within a short period of two months after the accident. However, those concentrations could be well compared with the values registered at the highly polluted Kerch Bight where a six years average for the period of monitoring prior the oil spill showed the same pollution levels (Table 6.2.10a).

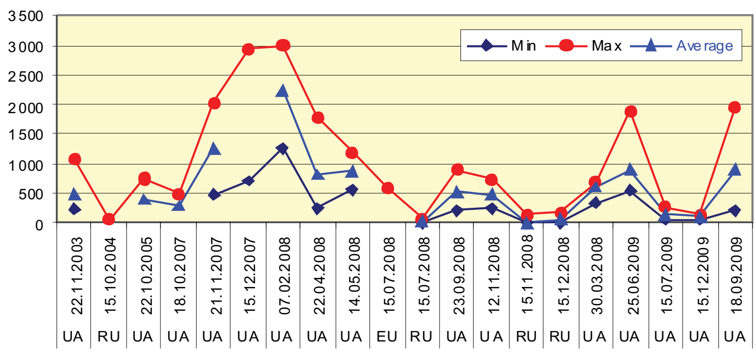

Fig. 6.2.10a. Temporal dynamics of total petroleum hydrocarbons concentration (µg/g) in the Kerch Strait bottom sediments in 2003–2009. UA — expeditions completed by Ukrainian Institutions, RU — Russian, EU — UNEP Expeditions. The data of IBSS in December 2007 and March 2008 were excluded from the figure due to unclear methodology of investigation and major disparity in general results obtained.

Data of the seabed pollution prior to the Kerch catastrophe are scarce; still, they clearly reveal the relatively high TPHs concentration levels in the range of 1–20 PC. The recorded levels are even higher than those registered in the second half of 2008 and in 2009. During the last years (2008–2009) petroleum hydrocarbons concentration in the Kerch Strait bottom sediments has stabilized at the level of 10–20 PC. Some periodical fluctuation is recorded and probably it is not connected with the seasonal factor but rather with sources of pollution.

Patchiness of petroleum pollution distribution remains yet a major problem for data collection and proper calculation of average parameters. The maxima registered close to the place of pollution source (the *Volgoneft-139* shipwreck) have revealed an increased level of TPHs presence after the accident which could be well expected. The accident was less reflected by averaged parameters and minimum concentrations to have shown their increase still after 11 November 2007. Importantly, the best evidence of the shipwreck place was given by a differently normalized data on polycyclic aromatic hydrocarbons. It is possible that normalized PAHs continued reflecting the Kerch Strait accident traces for long time after it happened (e. g. end of 2009).

However, it seems that the oil spill accident of November 2007 had shorter in time and more local in space consequences, especially as compared to permanently present pollution resulting from illegal transshipment and intense maritime traffic in the Kerch Strait waters. The Kerch Strait environment remains chronically polluted by petroleum hydrocarbons and the Kerch Strait accident contribution to it has been negligible for the Kerch Strait waters and sediments, in general.

Table 6.2.10a. Total petroleum hydrocarbons concentration (µg/g) in the Kerch Strait region bottom sediments.

No	Period	Min	Max	Average	The maximum patch location	Expedition, organization
UA	Monitoring, 2000–2006	–	–	3240	the Kerch Bight	YugNIRO, Kerch
UA	22 November 2003	230	1090 (22 PC)	490	the Kerch Strait, central part	YugNIRO, Kerch
RU	15 October 2004, Monitoring	–	59.5 (1.2 PC)	–	harbor of the port of Caucasus	SCHME BAS, Sochi
UA	22 October 2005		750 (15 PC)	400	the Kerch Strait	YugNIRO, Kerch
UA	18 October 2007		500 (10 PC)	300	the Kerch Strait	YugNIRO, Kerch
UA	November 2007	2790	6990 (140 PC)		the Kerch Bight	YugNIRO, Kerch
11 November 2007						
UA	21 November 2007		2024 (40.5 PC)	1250	the Kerch Strait	YugNIRO, Kerch
UA	December 2007 and March 2008	720	2925 (58.5 PC)		the Kerch port, southward of the Tuzla Island	MHI, Sevastopol
UA	December 2007	3	168 (3.4 PC)	66	the Kerch Strait	IBSS, Sevastopol
UA	March 2008	17	119 (2.4 PC)	52	the Kerch Strait	IBSS, Sevastopol
UA	7 February 2008		2988 (59.8 PC)	2250	the Kerch Strait	YugNIRO, Kerch
UA	22 April 2008	250	1780 (36 PC)	820	the Kerch Strait	YugNIRO, Kerch
UA	14 May 2008	568	1188 (24 PC)	890	the Kerch Strait	YugNIRO, Kerch
EU	July 2008, UNEP		600 (12 PC)		South of the Tuzla Island, the tanker crush place	UNEP Expedition
RU	24 July 2008	2.1	80.7 (1.6 PC)	18.08	westward of the Chushka Spit end	RosPrirodNadzor
UA	23 September 2008	220	900 (18 PC)	520	the Kerch Strait	YugNIRO, Kerch
RU	6–15 November 2008	0.0	139.2 (2.8 PC)	5.1	southward of the end of Chushka Spit	RosPrirodNadzor
UA	12 November 2008	250	740 (15 PC)	490	the Kerch Strait, central part	YugNIRO, Kerch
RU	December 2008	2.7	184.6 (3.1 PC)	54.3	South of the Tuzla Island	RosPrirodNadzor
UA	25 June 2009	540	1890 (38 PC)	900	the Kerch Strait, central part	YugNIRO, Kerch
UA	July 2009	70	275 (5.5 PC)	149	westward of the Tuzla Island	UkrSCES, Odessa
UA	December 2009	60	140 (2.8 PC)	102.6	westward of the Tuzla Island	UkrSCES, Odessa