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Pollution of the Caspian Sea

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Abstract The pollution of Caspian Sea waters and bottom sediments was described on the basis of long-term monitoring data from 1978 to 2004. It was shown that in the 1980s total petroleum hydrocarbons were in high concentration in the estuarine waters of the Ural River, in the western part of the North Caspian, and near the town of Izberbash on the Dagestan coast, but later they reduced drastically everywhere. In contrast to water in the bottom sediments, zones of high concentrations of petroleum hydrocarbons were located in shallow areas adjacent to the Volga delta and in the western part of the North Caspian, where fine sediments occurred. The other part of the North Caspian, with mainly coarse sediments, had rather clean bottom material. The high concentrations of phenols and detergents in the water occurred rather often at the beginning of the period but later decreased significantly. No seasonal trends and spatial features were observed in their distribution. The average concentration of ammonium was high in the estuarine areas of the Volga, Terek, and Sulak rivers. In water, among the chlorinated pesticides DDT dominated. All pesticides were much more abundant in the 1980s than in the 1990s. In the bottom sediments, pesticides accumulated near the Volga River delta and were practically absent in the central part of the North Caspian. The heavy metal concentration was in the range of regional background levels. In general, for all kinds of pollution studied for this area, there were marked small-scale patches in time and space of very high concentrations.

Keywords Detergents · Heavy metals · Monitoring · Pesticides · Petroleum hydrocarbons · Phenols · Pollution · Spatial and temporal variation

1 Introduction

Investigations into the pollution of the Caspian Sea, mainly of the petroleum hydrocarbons and their influence on the sea and coastal communities, began in the middle of the last century. But the systematic observations of dynamics of pollutants both in coastal areas of the sea, mostly subjected to anthropogenic influence, and in the open sea began only at the end of the 1970s after organization of a marine environment monitoring system, conducted by Hydrometeoservice of the Soviet Union. All chemical analysis was conducted in accordance to the standard guidance manuals [1, 2]. On the basis of the data from the State System of Monitoring (OGSN), assessments of the level of water pollution and description of seasonal and interannual variation were conducted each year [3–5]. The monitoring data became the basis of a general investigation of long-term balance and prediction of pollution of the Caspian Sea by petroleum hydrocarbons [6]. Detailed material of long-term scientific investigations of hydrological and morphological processes and the dynamics of polluting substances and sea level fluctuations on the increase pollution is described in monograph [7]. It gives information about the drainage and concentration of pollutants in the river water and in the suspended matters, their changes in time, and their influence on the condition of the North Caspian. The current data on hydrological processes and water pollution of the North Caspian during the winter period are also described in other articles [8–13].

2 Water Pollution of the North Caspian

In the period from 1978 to 1992 control of the water pollution of the North Caspian was conducted in the framework of the Soviet Union national program of seawater monitoring at the stations of five standard cross-sections (see Tuzhilkin and Kosarev, this volume). Besides temperature, salinity, and the concentration of dissolved oxygen and nutrients, determination of concentrations of ammonium, petroleum hydrocarbons, phenols, detergents, chlorinated pesticides (since 1985), and also heavy metals – mercury (since 1986), zinc and copper (since 1989) and lead (since 1990) was included. On the whole 3174 stations were employed. After stopping of the permanent monitoring investigations of water pollution in the shallow area of the North Caspian in 1992, this work was conducted by different expeditions in 1993–1996 and 2000–2002. The programs of the expeditions and the set of parameters of monitoring varied significantly, however, the data make it possible to describe the time dynamics and space distribution of pollution in water and bottom sediments. In the first expeditions and in 2000 the work was conducted in the summer period adjacent to the delta of the Volga River. The

expeditions in 2001 and 2002 covered both the estuarine part and the central part of the North Caspian. On the whole 444 stations were employed.

Total Petroleum Hydrocarbons

According to the monitoring data before 1992 the total petroleum hydrocarbons (TPHs) varied over a wide range and reached 3.78 mg/L in October 1984 at cross-section IIIa in the western part of the shallow area of the North Caspian. The average concentration of TPHs in the water column during this period was rather high and equal to 0.19 mg/L. The particularly high average concentration was observed before 1985. The later level of TPH pollution decreased considerably and mainly varied in the range 0.1–0.2 mg/L (Fig. 1). The spatial distribution of TPHs was patchy. The region in the northeastern part of North Caspian near the estuarine of the River Ural was the most polluted. The average values reached 1.2 mg/L. The level of pollution in the southwestern part of the investigated area near the border with coastal waters of Dagestan also increased. The pattern of seasonal variations of TPHs is not revealed (Table 1).

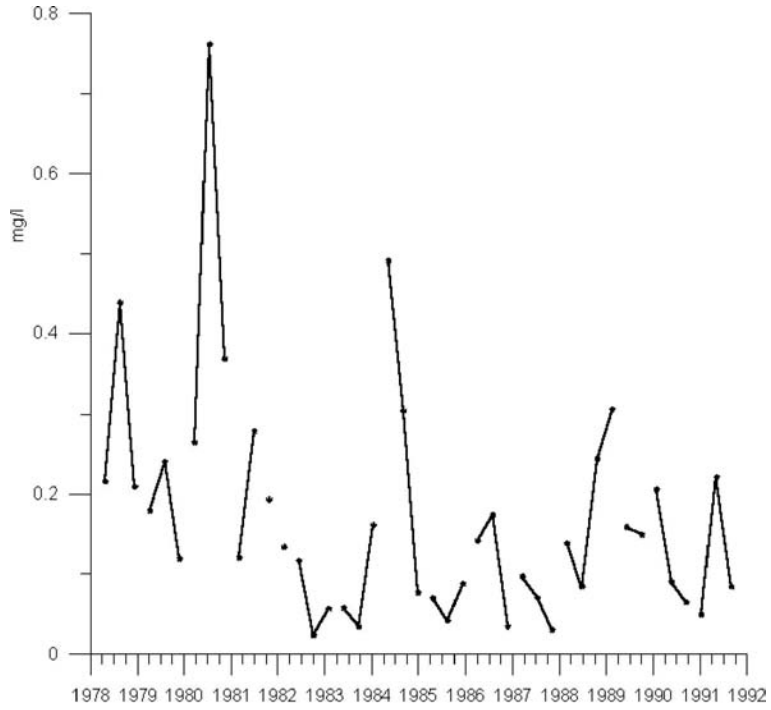

Fig. 1 Inter-annual variation of average concentration of TPHs (mg/L) in the waters of the North Caspian in 1978–1992

Table 1 Average monthly concentration of pollutants in the waters of the North Caspian in 1978–1992

Month	TPHs (mg/L)	Phenols (mg/L)	Detergents (mg/L)	NH_4 (mg/L)
February	0.11	0.002	0.041	54.8
March	0.31	–	0.016	21.4
April	0.28	0.005	0.049	43.8
May	0.05	0.007	0.039	21.9
June	0.14	0.007	0.066	35.6
July	0.13	0.002	0.032	14.3
August	0.25	0.005	0.071	53.1
September	0.29	0.009	0.063	44.3
October	0.13	0.005	0.042	25.8
November	0.08	0.005	0.028	8.8
December	0.35	0.001	0.026	–
Average annual concentration	0.19	0.005	0.054	37.2

In the period of 1993–2002 the average concentration of TPHs was 0.067 mg/L. This data corresponds to the investigations of 2001–2003 where average values changed from 0.029 to 0.073 mg/L [14], but were significantly less than KaspNIRKh estimation for the same period, which varied in the range 0.15–0.35 mg/L [15]. The maximum level 0.29 mg/L was reached at the end of June 2001 in the offshore part of the North Caspian at cross-section II. During the summer months of 1993–1996 the concentration of TPHs offshore of the sea side of the Volga River delta was rather low (Table 2). In summer 2000 the level of TPHs in the central part of the North Caspian was higher by several times than in autumn of the same year in estuarine part of the Volga. The next year water pollution reached the maximum level of that 10-year period. A high level was measured both in summer and in winter. The average for the estuarine part of the Volga was 0.105 mg/L, for cross-section II 0.267 mg/L, cross-section III 0.045 mg/L, and cross-section IIIa 0.035 mg/L. During the summer and autumn period of 2002 the concentration of TPHs in the water decreased sharply. Particularly high levels of pollution in the central part of the area in summer 2001 influenced the increase of spatial patchiness of the distribution of 10-year average levels (Fig. 2).

Phenols

During the period 1978–1992 the maximum concentration reached 0.048 mg/L, but usually it did not reach 0.02 mg/L. The average level for the North Caspian was 0.005 mg/L (Table 1). At the same time considerable seasonal variations in phenol concentrations in water were quite typical (Fig. 3). The

Table 2 Average concentration of pollutants in the waters of the North Caspian in 1993–2002

Pollutant (unit of concentration)	Year, Month, Region									
	1993 June Seaside of the Volga delta	1994 June Seaside of the Volga delta	1995 July–August Seaside of the Volga delta	1996 July–August Seaside of the Volga delta	2000 July North Caspian	2000 November Seaside of the Volga delta	2001 June North Caspian	2001 December Seaside of the Volga delta	2002 August Seaside of the Volga delta	2002 October North Caspian
TPHs (mg/L)	0.049	0.050	0.021	0.020	0.121	0.027	0.151	0.109	0.010	0.008
Phenols (mg/L)	–	–	–	–	–	0.003	–	0.003	–	0.008
Detergents (mg/L)	–	–	–	–	–	0.032	–	0.033	–	Less than DL*
NH_4, (μg/L)	490.3	203.7	204.8	–	192.6	–	701.2	74.7	30.8	14.0
DDT (ng/L)	0.300	0.353	0.175	0.110	–	–	–	–	–	0.244
DDE (ng/L)	0.050	0.073	0.043	0.025	–	–	–	–	–	0.010
DDD (ng/L)	0.069	0.090	0.020	0.007	–	–	–	–	–	less than DL**

*Detection limit 0.025 mg/L
**Detection limit 0.05 ng/L

Table 2 continued

Pollutant (unit of concentration)	Year, Month, Region									
	1993 June Seaside of the Volga delta	1994 June Seaside of the Volga delta	1995 July–August Seaside of the Volga delta	1996 July–August Seaside of the Volga delta	2000 July North Caspian	2000 November Seaside of the Volga delta	2001 June North Caspian	2001 December Seaside of the Volga delta	2002 August Seaside of the Volga delta	2002 October North Caspian
α-HCCH (ng/l)	0.070	0.108	0.080	0.029	–	–	–	–	–	3.460
γ-HCCH (ng/l)	0.030	0.034	0.025	0.006	–	–	–	–	–	1.394
Fe (μg/L)	–	–	–	–	–	35.6	–	32.2	–	24.0
Mn (μg/L)	–	–	–	–	–	3.6	–	3.0	–	1.3
Zn (μg/L)	–	–	–	1.1	–	5.6	–	4.5	–	7.1
Ni (μg/L)	1.3	–	0	0	–	2.1	–	2.1	–	2.4
Cu (μg/L)	1.2	1.2	0.1	0.1	–	3.1	–	2.8	–	4.3
Pb (μg/L)	0.15	0.1	0.1	0.1	–	4.9	–	4.1	–	0.5
Cd (μg/L)	0.1	0.1	0.1	0.1	–	0.7	–	0.5	–	0.2

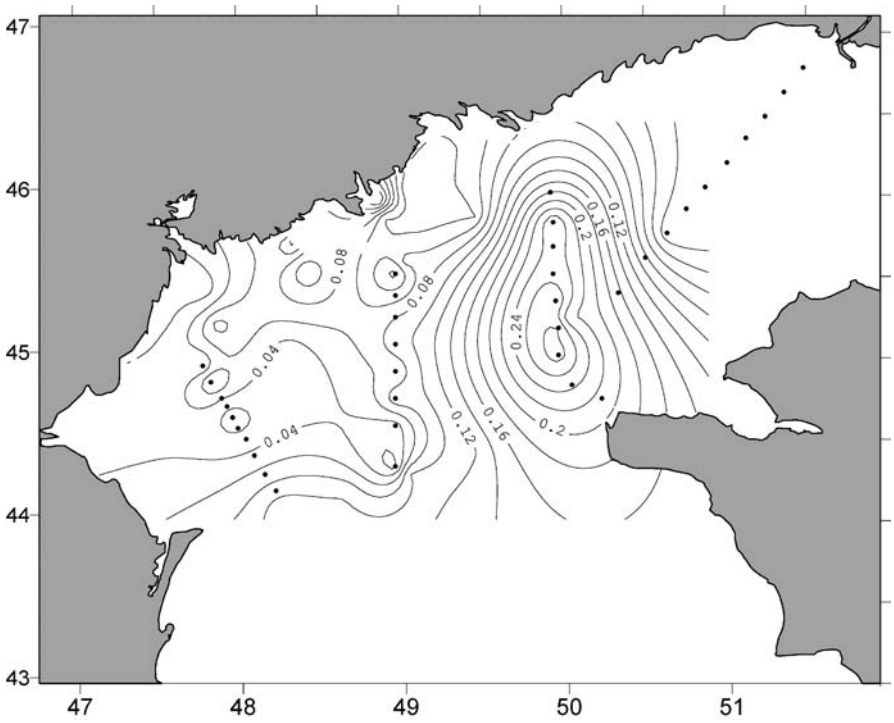

Fig. 2 Distribution of average concentration of TPHs (mg/L) in the waters of the North Caspian in 1993–2002

low levels of concentration are characteristic of the winter period. However, the number of measurements during this season was rather low and in January samples were not taken at all.

In autumn and winter 2000–2002 (Table 2) the average concentration of phenols in water was 0.005 mg/L. This coincides with the results of long-term monitoring. The maximum levels (0.017–0.018 mg/L) were measured in 2002 in the western part of the North Caspian in the zone of influence of the Volga discharge. On the whole, the level of the water pollution by phenols in the North Caspian is rather high.

Detergents

From 1978 till 1992 detergents was observed in 1745 samples taken in the frame of the monitoring programme in the waters of the North Caspian. The average concentration in the explored territory was 0.054 mg/L (Table 1). The higher values were measured in July–September, and the lower values in the cold period of the year. The highest values are more typical for the western part of the North Caspian.

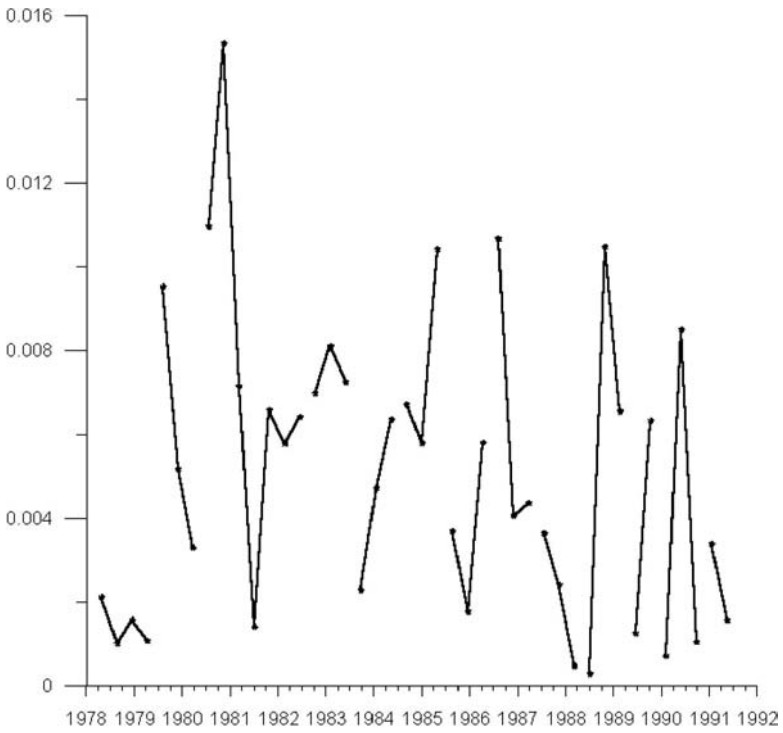

Fig. 3 Inter-annual variation of average concentration of phenols (mg/L) in the waters of the North Caspian in 1978–1992

The average concentration of detergents in November 2000 and December 2001 was 0.032 mg/L (Table 2). The maximum value reached 0.038 mg/L. In 2002 the concentration of detergents in the water was lower than the detection limit of the analytical method.

Ammonium

Until 1992 the average concentration of NH_4 was 37.2 μg/L and the maximum value was 897 μg/L. The higher values are typical for waters adjacent to the Volga delta (avandelta) in its western part. In the seasonal and interannual dynamics there is no clear regularity (Fig. 4, Table 1).

After 1992 the average concentration of NH_4 was 180.1 μg/L and was much higher than in the previous two decades (Table 2). The maximum value (2680 μg/L) was registered in August 2000 in the near-bottom layer in the western part of the North Caspian at cross-section IIIa. At the same time the average concentration of NH_4 in the surface layer (201.5 μg/L) was almost the same as in the near-bottom layer (233.5 μg/L). A slight difference in the vertical distribution of ammonia in the North Caspian was

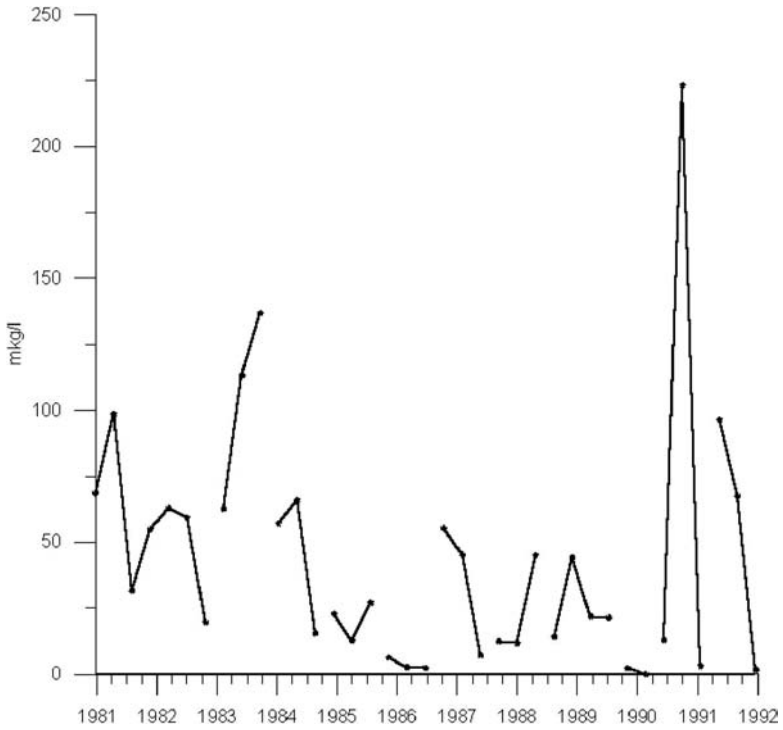

Fig. 4 Inter-annual variation of average concentration of ammonia (μg/L) in the waters of the North Caspian in 1978–1992

also observed in other years: in 2001 the average concentration in the surface layer was 510.5 μg/L and in the near-bottom layer 429.9 μg/L, in 2002 the values were 17.6 and 20.7 μg/L, respectively. This suggests that intensive mixture by wind in the shallow waters prevents stable vertical stratification of ammonia distribution. In general, the highest values occurred more often near the Volga delta and in the western part of the North Caspian.

Pesticides

From 1978 till 1992, of the chlorinated pesticides, DDT gave the highest concentration in water. The average value was 31 ng/L and the maximum value was 1950 ng/L in April 1985 in the eastern part of the North Caspian. DDE concentration was a great deal less than DDT and its average concentration was 1 ng/L. The maximum value (27 ng/L) was registered in June 1985 in the middle part of the area. The average concentration of α-HCH was 2 ng/L and the maximum value (85 ng/L) was measured in June 1991 in the eastern part of the North Caspian. For γ-HCH the average was 1 ng/L and the

maximum (264 ng/L) was observed in April 1985 in the eastern part of the North Caspian.

After 1992 the concentration of pesticides from the DDT group in the waters of the North Caspian was rather low and sometimes it was lower than the detection limit of the analytical method. The decade average and maximum values of DDT were 0.23 and 0.92 ng/L, respectively. For DDE the values were 0.03 and 0.21 ng/L, and for DDD they were 0.03 and 0.32 ng/L. On the whole, the concentration of pesticides of the DDT group was a little higher than at the beginning of the decade (Table 2). The average concentration of pesticides of the HCH group in the water was lower at the beginning of the given period. However, in October 2002 their concentration increased more than two orders of magnitude almost everywhere in the open waters of the North Caspian. The average and maximum values of α-HCH were 1.38 ng/L and 0.55 ng/L, respectively, and for γ-HCH 11.20 ng/L and 4.85 ng/L. These were observed in the surface layer at the border between the North and Middle Caspian. In general, the concentration of HCH isomers corresponded with the data from the waters in the eastern part of the North Caspian and in the area between the Volga and Ural rivers during the period of spring high water in 2003 and 2004, i.e., 10–40 ng/L and 7–15 ng/L, respectively [16].

Heavy Metals

Concentrations of metals in the water of the North Caspian was determined episodically in the period 1986–1991. The average value of mercury in the water was practically the same in the central and western parts of the area: 0.15–0.18 μg/L. The maximum value of 0.80 μg/L was registered in the middle of October 1986 at the most northerly station of cross-section IIIa. The average concentration of zinc and copper in the northwestern part of the North Caspian in 1989–1990 was 0.033 and 0.005 μg/L and the maximum value was 0.186–0.019 μg/L. The average concentration of lead in 1990 was 3.43 μg/L.

During the next decade (Table 2) the maximum concentration of heavy metals in the waters of the North Caspian were: iron 52 μg/L, manganese 5 μg/L, zinc 10.6 μg/L, nickel 4 μg/L, copper 6.2 μg/L, lead 8 μg/L, and cadmium 1 μg/L. On the whole, pollution of the waters of the central part of the North Caspian by heavy metals was much lower than in the northeastern part of the area in 2003–2004 [16]. Patches with high concentrations of heavy metals were not observed and the highest values of metals occurred in shallow waters both adjacent to the Volga delta and offshore. Temporal variation was not marked.

3
Bottom Sediments Pollution of the North Caspian

Total Petroleum Hydrocarbons

In bottom sediments near the delta of the Volga and shallow areas of the North Caspian the average concentration of TPHs in 1993–2002 was 13.6 μg/g and corresponded to background concentrations (from 2.81 to 18.56 μg/g) for the different natural complexes of the Russian part of the North Caspian in 2003 [17]. Single high values of TPHs in bottom sediments (higher than 35 μg/g) were registered repeatedly in navigable and fish-passing channels in avandelta of the Volga. It was here that in 1994 the maximum concentration (76.0 μg/g) was registered and the average value of this part was 15.1 μg/g (Table 3). The high level of pollution of bottom sediments by TPHs near the Volga delta and low background concentration in the rest of the vast middle part of the North Caspian caused considerable spatial heterogeneity in the distribution of average values and the appearance of local patches

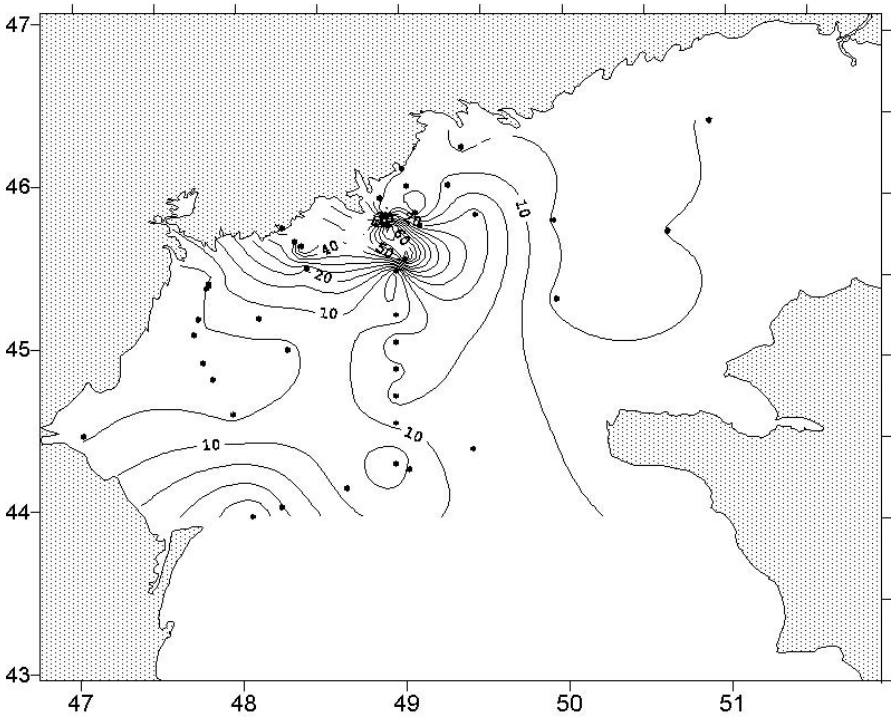

Fig. 5 Distribution of average concentration of TPHs (mg/g) in the bottom sediments of the North Caspian in 1993–2002

Table 3 Average concentration of pollutants in the bottom sediments of the North Caspian in 1993–2002

Pollutant (unit of concentration)	Year, Month, Region								
	1993 June Seaside of the Volga delta	1994 June Seaside of the Volga delta	1995 July–August Seaside of the Volga delta	1996 July–August Seaside of the Volga delta	2001 December Seaside of the Volga delta	2002 August Seaside of the Volga delta	2002 October North Caspian	CEP-2000* October Russian part of the North Caspian	CEP-2001* September Kazakhstan part of the North Caspian
TPHs, (μg/g)	30.0	17.9	10.8	10.0	15.4	14.0	4.8	1.57	11.56
Phenols, (μg/g)	–	–	–	–	–	–	0.49	–	–
DDT, (ng/g)	8.05	7.47	3.80	3.84	–	–	0.07	0.317	4.274 (pg/g)
DDE, (ng/g)	1.43	0.36	0.16	0.25	–	–	0.02	0.246	4.147 (pg/g)
DDD, (ng/g)	1.15	2.69	0.40	0.52	–	–	0.04	0.258	4.718 (pg/g)
α-HCH, (ng/g)	0.82	0.22	0.89	0.29	–	–	0.01	0.016	1.903 (pg/g)
γ-HCH, (ng/g)	5.30	0.96	0.93	0.70	–	–	0	0.173	2.268 (pg/g)

CEP-2000*, CEP-2001* – Caspian Environmental Program expeditions in the North Caspian [18].

Table 3 continued

Pollutant (unit of concentration)	Year, Month, Region								
	1993 June Seaside of the Volga delta	1994 June Seaside of the Volga delta	1995 July–August Seaside of the Volga delta	1996 July–August Seaside of the Volga delta	2001 December Seaside of the Volga delta	2002 August Seaside of the Volga delta	2002 October North Caspian	CEP-2000* October Russian part of the North Caspian	CEP-2001* September Kazakhstan part of the North Caspian
Fe (μg/g)	–	–	–	–	2723	–	3541	5873	6087
Mn (μg/g)	–	–	–	–	44.6	640.4	31.1	–	192.3
Zn (μg/g)	–	–	–	–	4.85	–	8.71	19.57	9.64
Ni (μg/g)	–	–	–	–	2.71	34.6	5.52	16.01	9.37
Cu (μg/g)	9.0	10.3	13.8	13.6	–	56.9	10.3	9.19	5.13
Pb (μg/g)	1.45	1.47	1.84	1.95	0.90	1.60	1.90	4.62	5.60
Cd, (μg/g)	0.05	0.49	0.09	0.09	0	0	0.081	0.060	0.047

*CEP-2000 and CEP-2001 Caspian Environmental Program expeditions in the North Caspian [18].

of high pollution (Fig. 5). Besides, slightly increased values were found in bottom sediments near the Dagestan shelf and in the eastern part of the North Caspian, according to the data from expeditions of the Caspian Environmental Program (Table 3). In the rest of the area the bottom sediments were not polluted by TPHs considerably. This coincides with the data showing decreasing pollutant concentrations in the sediments with predominating coarse fractions, which occupy the central part of the North Caspian [9]. The increased level of pollution in the shallow area adjacent to the Volga delta was evidently connected with the sinking to the bottom of thin fractions of suspended matter with adsorbed petroleum hydrocarbons. During storm mixing of the water, the thin fractions of bottom sediments are stirred-up and carried away by dominating western near-shore currents to the border with the Dagestan shelf. The spatial distribution of the zones with high concentrations of TPHs does not coincide in the water and in the bottom sediments.

Phenols

In Autumn 2002 the concentration of phenols in the bottom sediments varied from 0.183 to 0.888 μg/g and the average number was 0.489 μg/g. The increased values were observed in the central and western parts of the North Caspian.

Pesticides

The concentration of chlorinated pesticides in the bottom sediments in the North Caspian was rather high in 1993–1996. The average values of the DDT group was 5.89 ng/g. However, in autumn 2002 their concentration was rather low and the average value of DDT was only 0.07 ng/g and close to the detection limit of analytical method (Table 3). The average and maximum values of DDT in the North Caspian bottom sediments during the decade were 4.47 and 23.40 ng/g, respectively. Those for DDE were 0.31 and 3.20 ng/g, and those for DDD 1.18 and 11.00 ng/g. On the whole, the concentration of pesticides in the bottom sediments was in the range of values used in the QUASIMEME programme introduced for intercalibration of analytical laboratories [19]. The maximum values of concentration of all pesticides of the DDT group were observed at the end of June 1994, close to the sea side of the Volga delta. In general, the highest values of concentrations were observed in the shallow waters adjacent to delta where the polluted water of the river enters (Fig. 6). Upstream in the Volga delta the average values in 1993–1996 were 12.09 ng/g (DDT), 0.98 ng/g (DDE), 1.67 ng/g (DDD), 1.01 ng/g (α-HCH), and 2.77 ng/g (γ-HCH). These data correspond to the DDT concentrations observed in the water passages of the Volga in 1994, which were 4.4–26.3 ng/g [7].

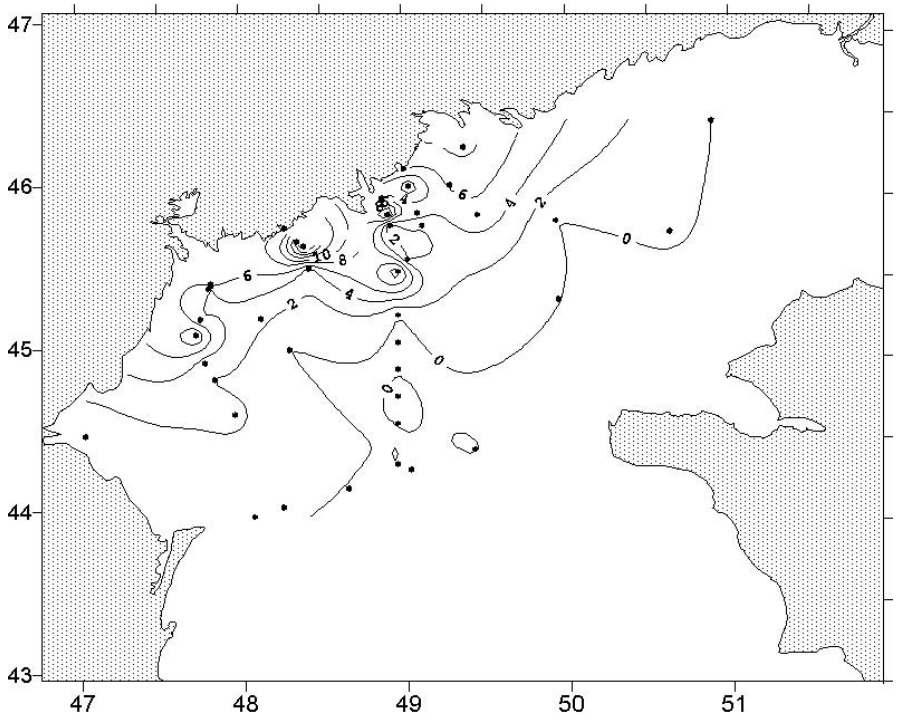

Fig. 6 Distribution of average concentration of DDT pesticides (ng/g) in the bottom sediments of the North Caspian in 1993–2002

The average concentration of the HCH group was rather high in 1993–1996; however, in October 2002 it only reached the detection limit of the analytical method in some samples (Table 3).

The maximum concentration of α-HCH was 3.45 ng/g in August 1995 in the western part of the area at the cross-section IIIa. The highest concentration of γ-HCH (14.20 ng/g) was registered in June 1993 in the part adjacent to the Volga delta. Similarly to DDT pesticides, the patches of high concentration of the HCH group were observed near the Volga delta (Fig. 7).

Heavy Metals

The concentration of heavy metals in the bottom sediments in the North Caspian was determined during the expeditions in 1993–1996 and in 2001–2002 (Table 3). The average concentration of iron was 3207 μg/g and a maximum value (13 900 μg/g) was registered in autumn 2002 in the offshore part of the area at cross-section IV. The main part of the iron data fell in the range from 930 to 5150 μg/g. On the whole, the iron concentration was higher in the offshore part of the area. The average concentration of manganese

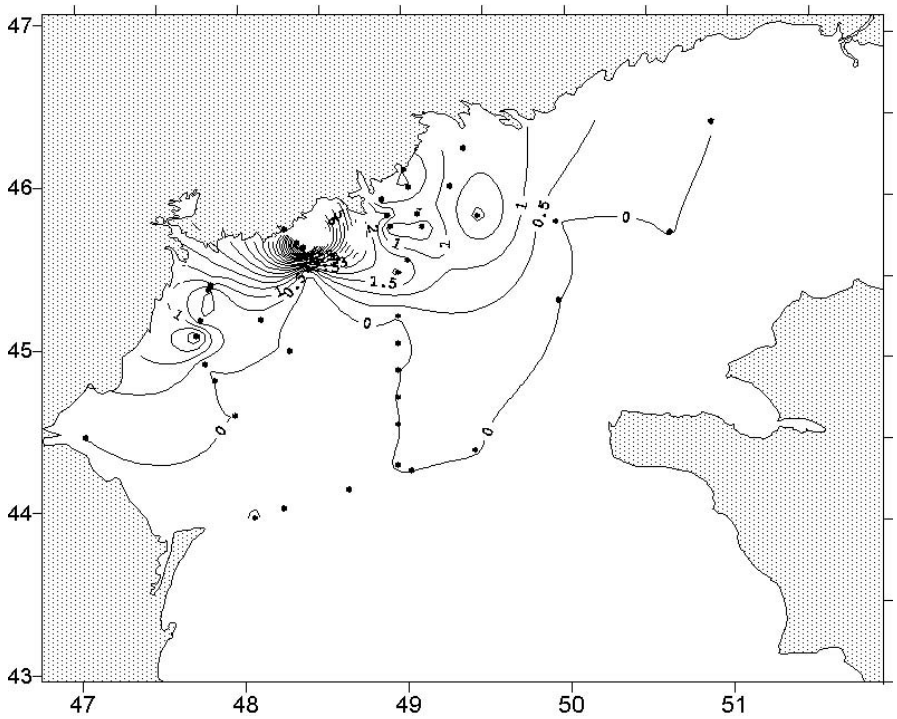

Fig. 7 Distribution of average concentration of γ-HCH pesticides (ng/g) in the bottom sediments of the North Caspian in 1993–2002

was 182.4 μg/g and the maximum value (1107.2 μg/g) was measured in summer 2001 in the shallow area near the Volga River delta. In contrast to iron, the manganese concentration in the bottom sediments near the Volga delta was more than ten times higher than in offshore part of the North Caspian (Fig. 8).

The average concentration of zinc was 7.13 μg/g and the highest value (33.8 μg/g) was registered in the offshore part of the North Caspian.

The average concentration of nickel was 11.7 μg/g and the maximum value (62.1 μg/g) was measured in the shallow area near the Volga River delta. In general, the concentration of nickel with an average of 34.6 μg/g was much higher in bottom sediments close to the delta than in the offshore areas of the North Caspian. The same feature characterizes the copper distribution. The bottom sediments near navigable waterway and fish passages were much more polluted by copper than in offshore areas of the North Caspian. The average value was 16.0 μg/g and maximum was 74.0 μg/g measured in August 2002 near the Volga delta.

The average concentration of lead was 1.61 μg/g and the maximum value (6.18 μg/g) was observed in June 1994 in the vicinity of the island Small

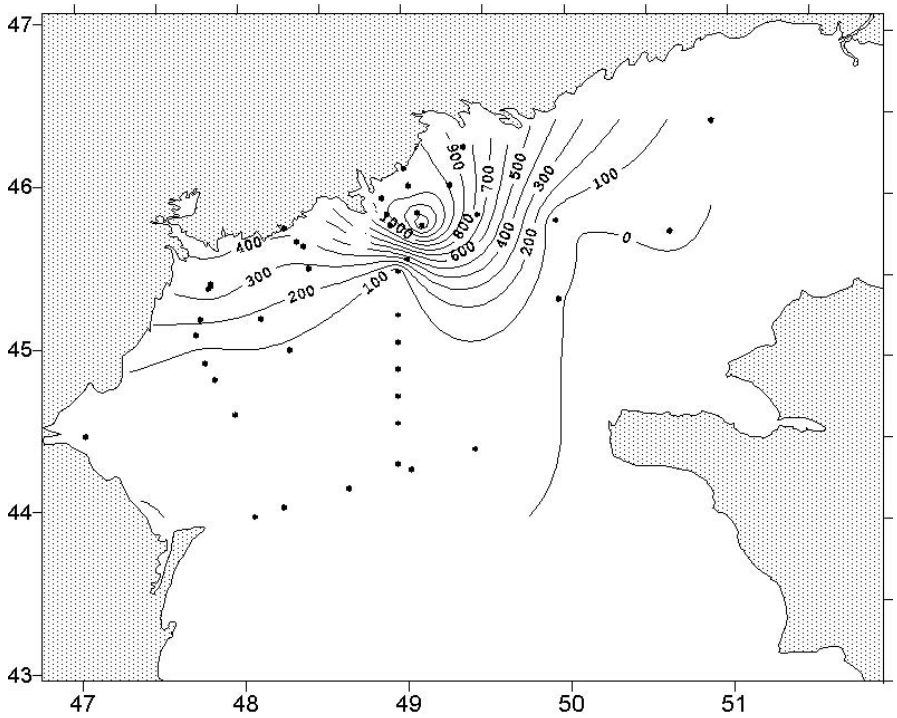

Fig. 8 Distribution of average concentration of manganese (μg/g) in the bottom sediments of the North Caspian in 1993–2002

Pearly. In general, the bottom sediments of the North Caspian are polluted by lead rather evenly.

The pollution of bottom sediments by cadmium is not considerable. Often its concentration was lower than the detection limit of the analytical method. The average concentration of cadmium was 0.061 μg/g and the maximum value was 0.291 μg/g.

The concentration of all heavy metals in the bottom sediments of the North Caspian, including the maximum values, did not exceed the range used for intercalibration in the programme QUASIMEME [19]. The expedition investigations carried out in 2001–2003 in the western part of the North Caspian showed significantly less concentrations of iron, manganese and copper; the same values were found for zinc and nickel, and much higher ones for cadmium and lead, in comparison with our data [14].

The results of monitoring expeditions in 1993–2002 correspond greatly with the data of the expeditions held under the Caspian Environmental Programme (CEP) in 2000–2001 (Table 3) [18]. During those expeditions the increased values of iron concentration in bottom sediments were registered both in deep and eastern parts of the North Caspian. The manganese and

nickel concentrations were higher in the adjacent part of the Volga delta as well as in the eastern part, in comparison with the other areas. The copper content was high near the Volga delta and low in the eastern part. The bottom sediments of the North Caspian were polluted by lead and cadmium rather evenly.

4
Dagestan Coastal Waters

In the frame of the routine national monitoring programme pollution of the Dagestan coastal waters was measured in 1978–2004 at 36 stations placed in eight shallow parts in the vicinity of the towns of Lopatin, Makhachkala, Kaspyisk, Izberbash, and Derbent and in estuarine areas of the Terek, Sulak, and Samur rivers, and at two standard cross-sections at a central part of the sea from Chechen' Island to Mangyshlak peninsula and from the town of Makhachkala to Cape Sagunduk (Fig. 1). Standard hydrological and hydrochemical parameters – temperature, salinity, dissolved oxygen and nutrients, and concentrations of ammonia, total petroleum hydrocarbons, phenols and detergents (till 1991) were studied in the monitoring programme.

Total Petroleum Hydrocarbons

The average concentration of TPHs in the water for the whole period was 0.076 mg/L. In these shallow areas different layers were polluted rather equally. For the upper layer the average was 0.080 mg/L, for the medium it was 0.076 mg/L, and in the near-bottom water layer TPH content was 0.072 mg/L. The maximum concentration reached 1.81 mg/L in the upper layer, in mid-March 1989 in an area near the town of Izberbash. In general, this area was most polluted (Table 4). The increased average TPH concentrations were also measured in estuarine areas of the Terek River and near the town of Derbent. In contrast, open waters of the Middle Caspian, the estuarine area of the Samur River, and waters near the town of Kaspyisk were rather clean. Interannual variation of water pollution by TPHs at the Dagestan shelf showed clear evidence of its reduction during recent years (Figs. 9, 10). Within the last decade the high average concentrations were measured only in the estuarine region of the Terek River and near the village of Lopatin.

The seasonal dynamic of TPH content in waters of the Dagestan shelf is not clear (Table 5). The monthly average values were rather similar. A slight increase could be seen in the first part of the year. It is suggested that decreasing TPH concentrations in the upper layer in the warm part of the year is followed by an increase in the speed of degradation of petroleum hydro-

Table 4 Mean values of pollutants in different regions of the Dagestan coastal waters and at the cross-sections in the Middle Caspian during 1978–2003

Region	TPHs mg/L	NH_4 μg/L	Phenols mg/L	Detergents mg/L
Lopatin town	0.076	110	0.006	0.056
Terek River	0.084	101	0.007	0.064
Sulak River	0.074	100	0.006	0.065
Makhachkala town	0.070	90	0.006	0.062
Kaspyisk town	0.068	86	0.005	0.060
Izberbash town	0.094	89	0.007	0.061
Derbent town	0.086	90	0.006	0.066
Samur River	0.069	90	0.006	0.058
Cross-section Chechen-Mangyshlak	0.063	66	0.004	0.053
Cross-section Makhachkala-Sagunduk	0.080	62	0.005	0.043
Average for all regions	0.076	91	0.006	0.060

carbons due to the high temperature of air and water. This seasonal feature is clear in the most polluted part of the Dagestan shelf near the town of Izberbash. Here the maximum TPH concentration was in December–March and the minimum in June–October. Also, the same seasonal variation was typical for the estuarine regions where the maximum occurred in November and February.

Phenols

The concentration of phenols in the waters of the Dagestan shelf varied from 0 to 0.095 mg/L and the average was 0.006 mg/L (Table 4). It was slightly increased in the Terek River estuarine region and near the town of Izberbash. Some values were ten times or more higher than others. These peaks were noted in monitoring investigations during 1978–2004 in all parts of Dagestan shelf as well as in all seasons. One could suggest that phenols polluted waters in different parts of the Dagestan shelf rather uniformly (Figs. 11, 12). Interannual variation indicated the reduction of phenols concentrations in recent years down to 0.003–0.004 mg/L. The seasonal dynamic is not clear. The minimum (0.004 mg/L) was noted in March and December and the maximum (0.010 mg/L) was in June, mainly due to very high values in 1978.

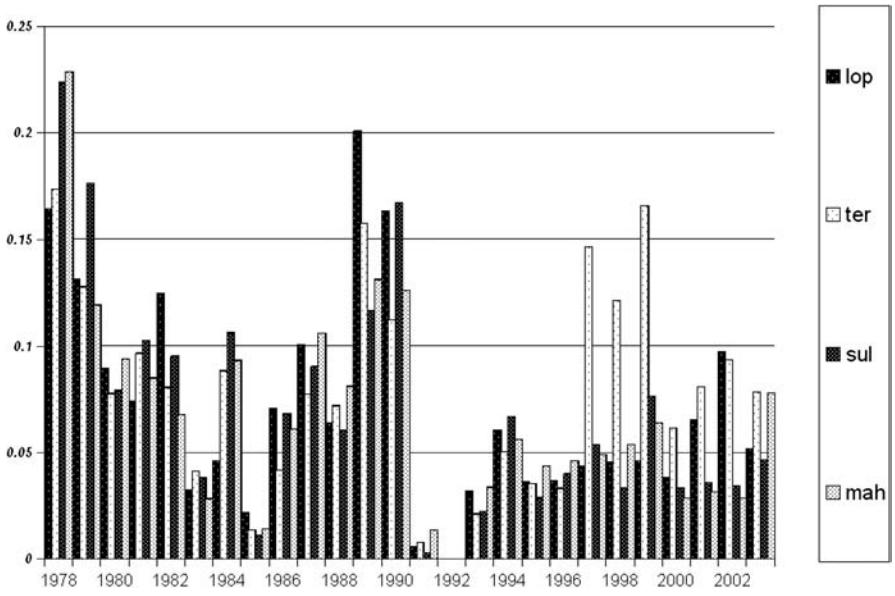

Fig. 9 Inter-annual variation of total petroleum hydrocarbons (mg/L) in the Dagestan coastal waters near Lopatin (*lop*), Makhachkala (*mah*), and estuarine areas of the Terek (*ter*) and Sulak (*sul*) rivers during 1978–2003

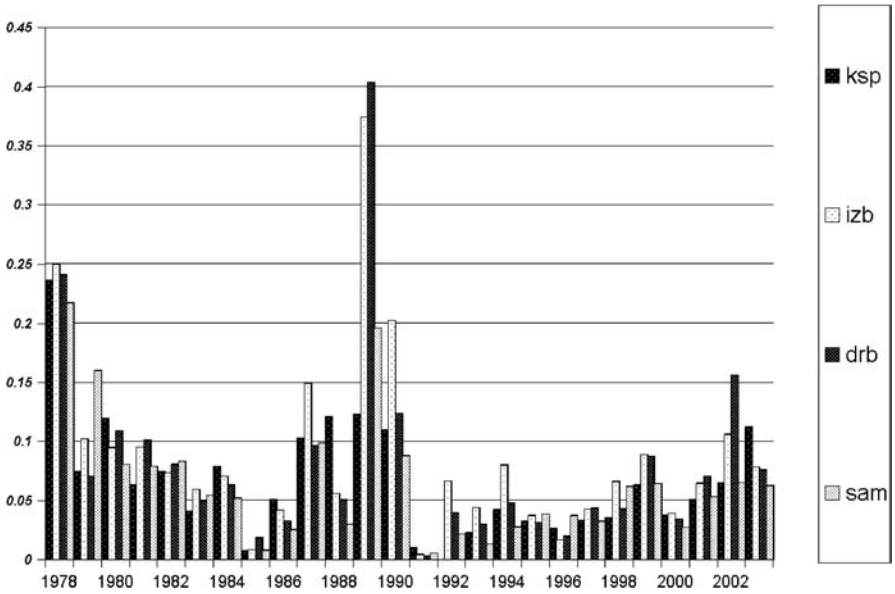

Fig. 10 Inter-annual variation of total petroleum hydrocarbons (mg/L) in the Dagestan coastal waters near Kaspyisk (*ksp*), Izberbash (*izb*), Derbent (*drb*), and estuarine area of the Samur River (*sam*) during 1978–2003

Table 5 Monthly average concentration of total petroleum hydrocarbons (mg/L) in the waters of the Dagestan shelf in 1978–2004

Region	Month											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Lopatin town	0.087	0.082	0.088	0.062	0.072	0.070	0.045	0.069	0.090	0.083	0.111	0.049
Terek River	0.081	0.119	0.081	0.113	0.091	0.068	0.068	0.081	0.079	0.073	0.174	0.113
Sulak River	0.070	0.112	0.065	0.071	0.091	0.061	0.059	0.069	0.076	0.074	0.132	0.072
Makhachkala city	0.079	0.080	0.073	0.093	0.076	0.039	0.065	0.052	0.071	0.062	0.063	0.040
Kaspyisk town	0.068	0.116	0.043	0.064	0.063	0.078	0.067	0.048	0.088	0.066	0.074	0.094
Izberbash town	0.134	0.223	0.137	0.084	0.093	0.045	0.056	0.053	0.105	0.053	0.047	0.118
Derbent town	0.053	0.186	0.099	0.089	0.111	0.141	0.055	0.072	0.130	0.055	0.027	0.050
Samur River	0.056	0.168	0.087	0.099	0.096	0.049	0.049	0.053	0.080	0.036	0.029	0.035
Cross-section Chechen-Mangyshlak	–	0.077	0.036	0.082	–	–	–	0.069	0.064	0.045	0.041	0.040
Cross-section Makhachkala-Sagunduk	–	0.091	–	0.096	0.012	–	–	0.063	0.045	0.042	0.090	0.042
Average for all regions	0.081	0.108	0.080	0.087	0.083	0.061	0.060	0.064	0.085	0.064	0.068	0.061

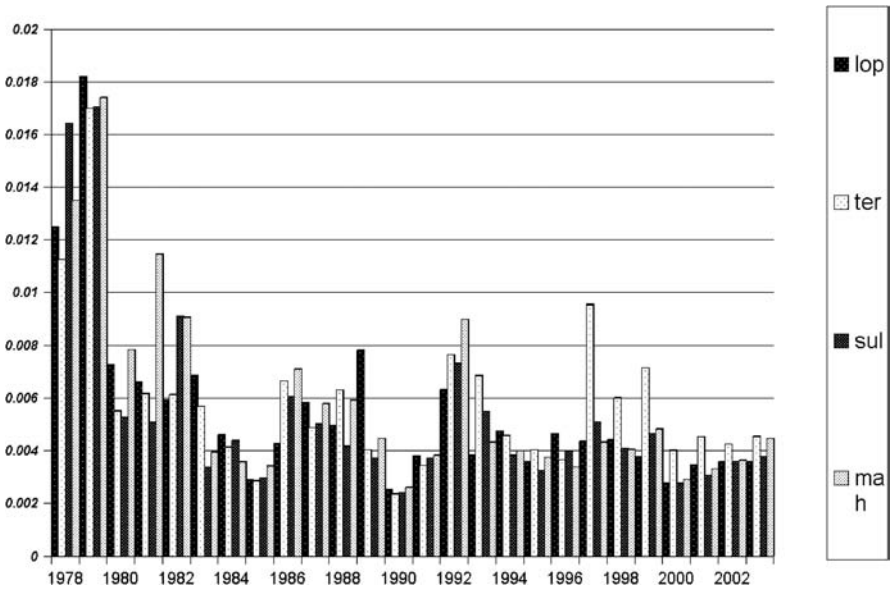

Fig. 11 Inter-annual variation of phenols (mg/L) in the Dagestan coastal waters near Lopatin (*lop*), Makhachkala (*mah*), and estuarine areas of the Terek (*ter*) and Sulak (*sul*) rivers during 1978–2003

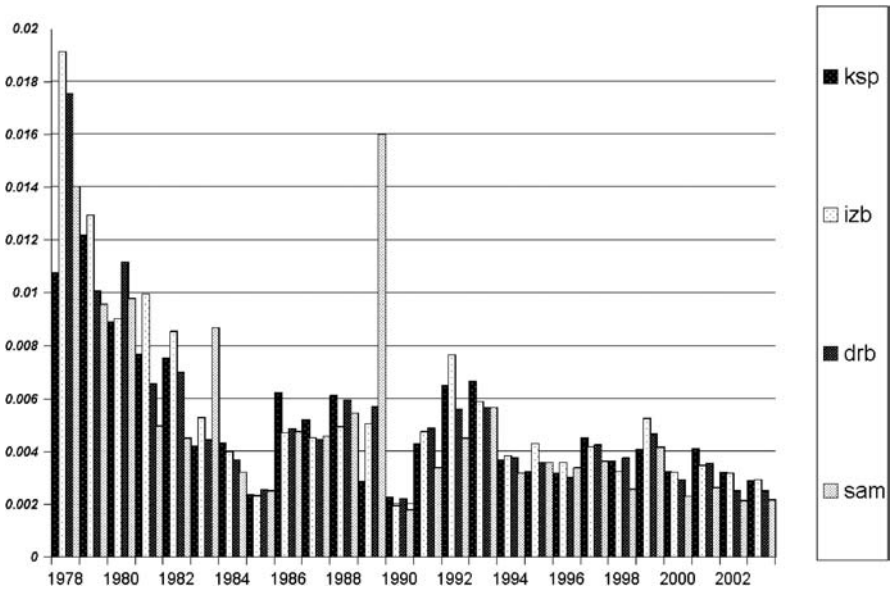

Fig. 12 Inter-annual variation of phenols (mg/L) in the Dagestan coastal waters near Kaspyisk (*ksp*), Izberbash (*izb*), Derbent (*drb*), and estuarine area of the Samur River (*sam*) during 1978–2003

Detergents

The average concentration of detergents from 1978 to 1991 was 0.060 mg/L (Table 4). The maximum value (0.58 mg/L) occurred in waters of the Sulak River estuarine area and near Lopatin in 1979 and 1981. Slightly lower concentrations were measured practically everywhere on the Dagestan shelf. In general, increased content of detergents in the water was typical for estuaries. The open sea water was less polluted in comparison with coastal waters. Monthly average concentrations varied within a narrow range from 0.044 mg/L in June to 0.073 mg/L in February. The seasonal variation was not marked. On the long-term scale, the content of detergents in the water was highest in the 1970s and reduced in the 1990s.

Ammonium

The average concentration of NH_4 was 90.9 μg/L. The maximum content reached 1970 μg/L in September 2001 near Lopatin. The increased content of ammonia was typical for the estuarine waters of the Terek and Sulak rivers and also for the northern part of the Dagestan shelf (Table 4). At the same time the open waters were characterized by low ammonia concentration. The seasonal dynamic of ammonium showed a rather clear increase of average values in January–March (120–130 μg/L) and June (145 μg/L), and a following decrease in August–October (65–77 μg/L). The same seasonal fluctuation was described earlier; but the winter concentration was higher (200–300 μg/L) [20]. In the long-term variation there were two maximum values in 1978 and 1982. Later, the content of NH_4 in waters almost everywhere dropped to about 50 μg/L and slightly increased only in since 2000 (Figs. 13, 14).

5
Water Pollution of the South Caspian

The description of pollution of the South Caspian is based on data from routine monitoring programmes [4, 5] and from investigations carried out by the Academy of Science of Azerbaijan [21]. The main part of the studies was carried out at standard cross-sections of the Hydrometeoservice of the Soviet Union, with some additional stations during 1978–1995. The samples were taken and treated by standard methodology in accordance with the Guidelines [1, 2].

The seasonal dynamic of water pollution in the South Caspian clearly indicated increasing concentrations of petroleum hydrocarbons in the direction from east to west. The average concentrations in winter were 0.15, 0.14, and 0.19 mg/L in eastern, central, and western parts of the region, respec-

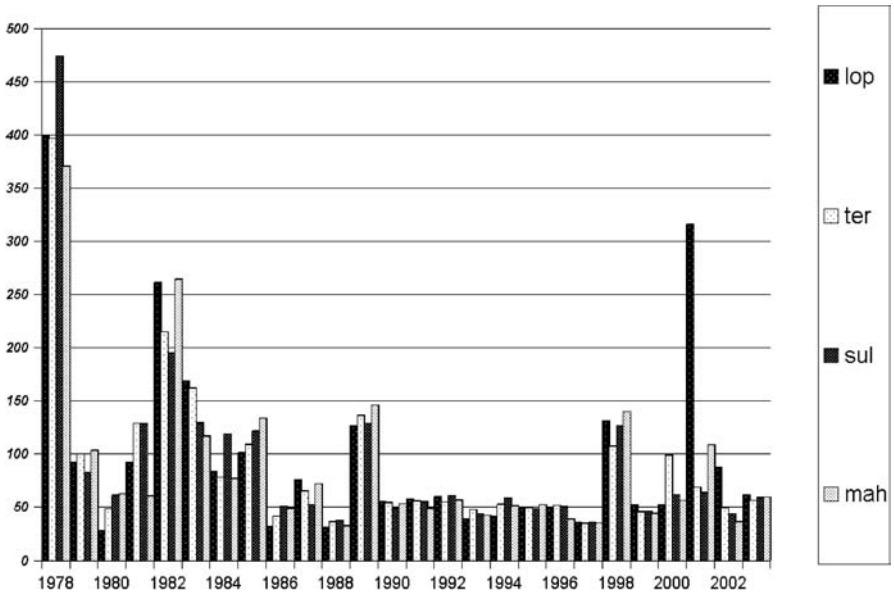

Fig. 13 Inter-annual variation of NH_4 (μg/L) in the Dagestan coastal waters near Lopatin (*lop*), Makhachkala (*mah*), and estuarine areas of the Terek (*ter*) and Sulak (*sul*) rivers during 1978–2003

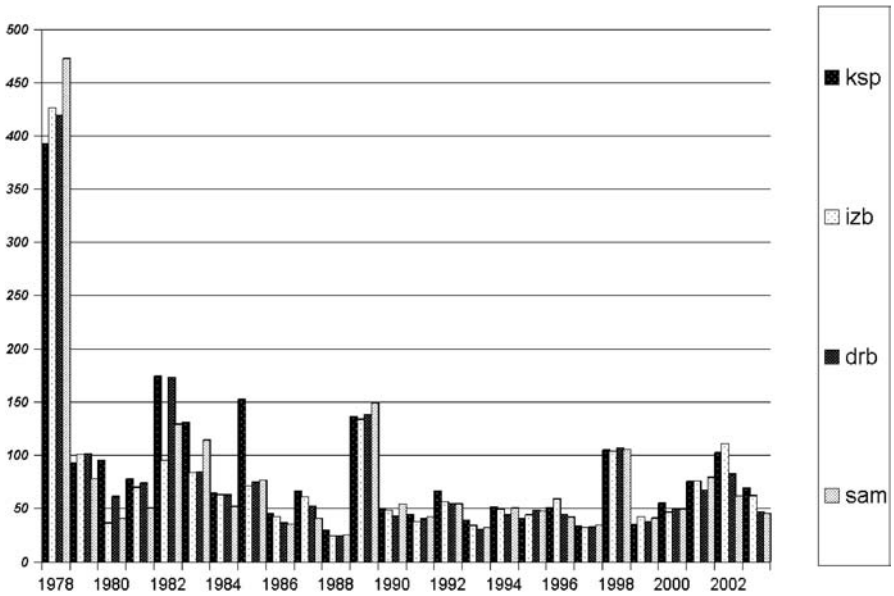

Fig. 14 Inter-annual variation of NH_4 (μg/L) in the Dagestan coastal waters near Kaspyisk (*ksp*), Izberbash (*izb*), Derbent (*drb*), and estuarine area of the Samur River (*sam*) during 1978–2003

tively. The same features were seen with the spatial distribution of phenols (0.005, 0.005, and 0.008 mg/L) and detergents (0.04, 0.02, and 0.09 mg/L) (Fig. 15).

In spring, concentration of TPHs, phenols and detergents in the upper layer of the South Caspian waters also increased towards the western shelf: 0.08, 0.08, and 0.15 mg/L; 0.006, 0.002, and 0.007 mg/L; and 0.03, 0.01, and 0.08 mg/L, respectively. The pollution was lowest in the central part of the region .

In summer the main features of pollution distribution remained the same. The western part was polluted much more than the others. The average value for this season's concentration was 0.07, 0.07, and 0.16 mg/L for TPHs; 0.006, 0.001, and 0.006 mg/L for phenols; and 0.02, 0.01, and 0.07 mg/L for detergents .

In autumn, along with decreasing temperature, the TPHs concentrations increased (0.12, 0.10, and 0.16 mg/L), but remained practically at the same level for phenols (0.006, 0.003, and 0.006 mg/L) and for detergents (0.035, 0.011, and 0.08 mg/L).

In general, waters of the South Caspian could be considered as heavily polluted. Usually the highest concentrations of petroleum hydrocarbons occurred near the Neftyanye Kamni Bank, Baku Bight (the maximum value reached 1332–1364 mg/L), in the estuarine region of the Kura River near Turkmenbashy (the average concentration was 0.16–0.27 mg/L) and Cheleken. Relatively clear coastal waters were near the town of Nabran (0.07–0.18 mg/L), in the Lenkoran area (0.08–0.17 mg/L) and in the estuary of the Sefidrud River in Iran (0.05–0.1 mg/L) [4, 22].

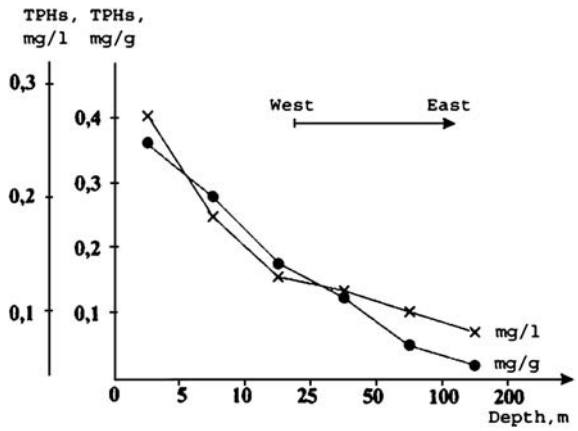

Fig. 15 Reduction in concentration of petroleum hydrocarbons in water (mg/L) and bottom sediments (mg/g) with increasing depth, in the direction from west to east in the Azerbaijanian part of the South Caspian [9]

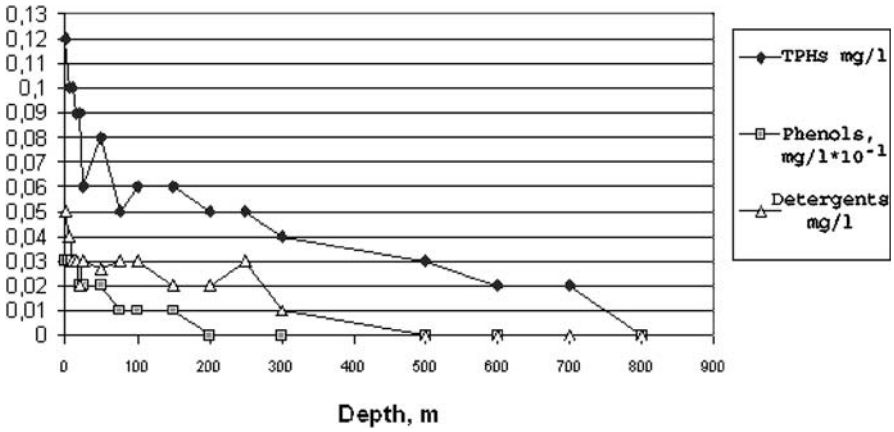

Fig. 16 Decreasing concentration of petroleum hydrocarbons (mg/L), phenols (mg/L $\times 10^{-1}$), and detergents (mg/L) with increasing depth in 1978–1995 [9]

In the Caspian, the concentration of pollutants in waters decreased with depth. The content of petroleum hydrocarbons, phenols, and detergents fell from the maximum value in the surface layer to "zero" in the layer at 500–1000 m (Fig. 16).

6
Bottom Sediments Pollution of the South Caspian

The upper horizons of bottom sediments of the South Caspian were significantly polluted by petroleum hydrocarbons. The thickness of the polluted layer varied from only several centimeters in the areas with negative sedimentation to 8–10 m in some parts of the Baku Bight. These sediments had dark-gray and sometimes even black color and consisted of a friable mixture of detritus with shells and masut, crude oil and mud. The content of petroleum components in sediments of the Baku Bight is mainly represented by resinous-asphalten fractions (60%) and heavy fractions of hydrocarbons like $C_{10} - C_{12}$ (2.0%) and $C_{13} - C_{20}$. The concentration of petroleum hydrocarbons in the shallow areas of the South Caspian varied in a wide range from zero to 226 mg/g and the average value was 1.52 mg/g (Table 7). The western shelf has much higher concentrations of TPHs (the average value was 2.5 mg/g) than the eastern shelf (0.21 mg/g). The average concentration of petroleum hydrocarbons in sediments north of the Apsheron Peninsula was 0.71 mg/g and near the Neftyanye Kamni Bank 0.76 mg/g. Inside the Baku Bight the concentration was very high and reached 95.1 mg/g, near the Sanchagal it was 0.94 mg/g, and in the shallow Makarov Bank 0.81 mg/g. Other parts of the western shelf, like areas near the Nabran, Zuria, Andreev Bank,

Table 6 Concentration of petroleum hydrocarbons (mg/g) in different layers of the bottom sediments in the South Caspian [9]

Region	Depth of sampling place (m)	Hydrocarbon concentration Range of sampling 0.0 (mg/g)	0–0.3 m (mg/g)	0.3–0.5 m (mg/g)	0.5–0.7 m (mg/g)	0.7–1.0 m (mg/g)	Type of sediment
Aktau	5.0	0.21	0.15	0.11	0.08	0.03	Mud
Turkmenbashy	4.0	2.4	1.94	1.85	1.77	1.6	Mud
Cheleken	3.0	0.3	0.20	0.16	0.13	0.11	Sand
Okarem	5.0	0.13	0.11	0.09	0.07	0.03	Mud

and Kurinsky Kamen were much cleaner. TPH average concentrations in bottom sediments in these regions were only 0.03, 0.04, 0.15, and 0.07 mg/g, respectively. At the eastern shelf the level of pollution by petroleum hydrocarbons was rather low and reached 0.19 mg/g in Aktau harbor and 0.35 mg/g in Turkmenbashy Bay [4].

In deep parts of the South Caspian the bottom sediments were rather clean. The shallow areas in the Azerbaijanian part were more polluted and decreasing TPH concentrations corresponded to increasing depth (Fig. 15).

Over the whole Caspian Sea the place most polluted by petroleum hydrocarbon sediments is the Baku Bight. The limited water exchanges with the open sea and long-term dumping of different kinds of wastes, industrial and municipal garbage are the main reasons for appearance the of "anthropogenic" sediments in the bight. Due to stirring of sediments during the stormy weather, or dredging of the bottom materials in harbor, or dumping of sediments from the bight into the sea, the secondary pollution of water occurs rather often. In contrast to the Baku Bight, in shallow areas influenced by waves, and in places with strong near-bottom currents, the sedimentation of thin particles with adsorbed pollutants was strongly limited and consequently the bottom sediments were rather clean. For instance, such areas were noted near the Apsheron threshold, in the vicinity of the Zhiloi Island, and the Neftyanye Kamni Bank (Neft Dashlaru) [4, 23].

In the special places for dumping of materials dredged for industrial and shipping interests the concentration of petroleum hydrocarbons increased. In such a place north of the Apsheron Peninsula the average TPH concentration was 0.14 mg/g. Near Apsheron it was 0.15 mg/g, not far from city Baku 0.36 mg/g, near Karadag 0.24 mg/g, near Aktay 0.12 mg/g, near Bekdash 0.16 mg/g, near Kianly 0.17 mg/g, near Turkmenbashy 0.16 mg/g, near Cheleken 0.15 mg/g, and near Okarem it was 0.30 mg/g [9].

In all polluted areas of the sea the concentration of petroleum hydrocarbons quickly decreased towards the inside of the bottom sediments (Table 6).

Table 7 Size fraction of bottom sediments and concentrations of pollutants in the South Caspian in 1978–1994 [5]

Depth (m)	TPHs, (mg/g)	Phenols (μg/g)	Hg, (μg/g)	Fraction %						Type of bottom sediments
				< 0.005 mm	> 2.0 mm	> 0.5 mm	> 0.25 mm	> 0.1 mm	< 0.005 mm	
Western shelf										
0.0	0.01					53.6				Gravely sand
0–5.0	0.04						72.4			Coarse sand
0.0–1.5	0.09							75.0		Medium sand
0.5–10.0	0.22							82.1		Small sand
0.5–10.0	0	0.32	1.4							Dusty sand
0.5–10.0	0.06	LDL*	1.0	46.0						Clay
0.5–10.0	0.2	0.25	1.2	18.0						Clayey soil
0.5–10.0	0.14	0.09	0.7	8.8						Sandy soil
0.5–10.0	19.0	0.68	0.6	8.2						Sandy mud
0.5–0.25	20.2	1.1	0.7	22.3						Clayey soil mud
0.5–50.0	24.0	1.5	0.74	54.0						Clayey mud
Eastern shelf										
1.0	0.15	0.2	0.32					78.1		Small sand
3.0–10.0	0.20	0.45	0.10						52.5	Dusty sand
10.0	0.93	0.34	0.20	7.6						Sandy mud
5.0–25.0	0.50	0.65	0.32	26.4						Clayey soil mud
5.0–50.0	0.84	1.15	0.44	45.5						Clayey mud
5.0–10.0	0.01	0.0	0.0	43.0						Clay
5.0–10.0	0.12	1.0	–	25.5						Clayey soil

* Less than detection limit

The pollution stopped in clay and clayey soil that was covered with modern sediments consisting of sand and mud.

Among important conditions like distance from the source, depth of place or near-bottom currents, which influence the concentration of pollutants in bottom sediments, the size spectrum of particles in sediments is also of great importance. A predominance of fine fractions leads to increasing concentrations of petroleum hydrocarbons in sediments, e.g. in sand the concentration of TPHs increased from gravel (0.01 mg/g), to coarse (0.04 mg/g), medium (0.09 mg/g), small (0.18 mg/g), and dusty (0.26 mg/g) fractions (Table 7). The same tendency was marked in clay sediments: the petroleum content was 9.6 mg/g in sandy clay, somewhat higher (10.3 mg/g) in clayey soil, and reached the maximum value (12.3 mg/g) in clayey mud. In the Baku Bight a high concentration was measured in the mud (103.8 mg/g) in comparison with the sand (0.75 mg/g) and clay (0.21 mg/g).

The long-term variations clearly indicate a reduction of pollution level (Table 8). It could be the result of increased seawater level and falling industrial activity in the region as a whole.

On the whole, the concentration of heavy metals in bottom sediments did not exceed the regional background value. The most clear exception is Baku Bight where the concentration of mercury in bottom sediments had an average of 1.3 mg/g, for nickel it was 41.3 mg/g, and for strontium 330.3 mg/g.

Table 8 Long-term variations in concentration of petroleum hydrocarbons (mg/g) in bottom sediments of the South Caspian in 1978–1994

Year	Hydrocarbon concentration		
	Western Shelf	Eastern shelf	Baku Bight
1978	2.0	1.0	92.5
1979	1.8	1.2	86.4
1980	0.9	1.0	90.0
1981	0.7	0.92	70.5
1982	0.33	0.59	42.5
1983	0.93	0.68	28.4
1984	0.55	0.71	50.3
1985	1.6	0.57	98.0
1986	1.3	0.38	40.0
1987	1.0	0.21	20.2
1988	0.79	0.19	36.3
1989	0.37	0.14	24.5
1990	0.67	0.10	12.5
1991	0.42	0.09	5.2
1992	0.28	0.08	4.0
1993	0.18	–	0.84
1994	0.11	–	0.75

Table 9 Average concentration of pollutants in bottom sediments of Baku Bight in 1978–1995

Depth (m)	TPHs (mg/g)	Organic substances (mg/g)	Phenols (mg/g)	Cu (μg/g)	Pb (μg/g)	Ni (μg/g)	V (μg/g	Be (μg/g)	Sr (μg/g)	Cr (μg/g)	Hg (μg/g)
0.0–0.25	68.4	86.5	0.0015	35.7	24.5	43.1	56.5	1.2	350.0	407.0	1.3
0.25–0.5	78.0	90.5	0.001	33.8	22.8	41.3	59.3	1.1	363.0	421.6	1.4
0.5–0.75	36.4	50.6	0.0008	32.5	20.3	38.4	52.2	1.2	183.7	360.3	1.2
0.75–1.0	28.9	44.8	0.002	28.7	18.0	28.0	51.5	1.0	160.0	361.7	1.0
1.0–1.5	17.1	22.0	0.0006	23.0	13.4	24.1	40.7	1.0	207.5	250.7	0.6
1.5–2.0	6.8	7.7	0.0001	17.0	10.1	14.5	30.4	1.0	LDL*	166.7	0.05
2.0–2.5	2.1	3.4	0.00005	12.8	9.4	7.9	28.4	1.0	LDL*	127.8	0.13
2.5–3.0	1.4	1.8	0.0007	12.1	9.4	5.7	24.7	1.0	LDL*	93.4	0.10
3.0–3.5	0.9	1.9	LDL*	9.7	6.6	5.0	17.5	1.0	LDL*	46.2	0.3
3.5–4.0	0.8	1.0	LDL*	9.5	3.0	5.0	15.1	1.0	LDL*	31.8	LDL*
4.0	0.6	0.8	LDL*	8.8	1.7	5.0	14.0	1.0	LDL*	27.1	LDL*
Average	22.0	28.2	0.007	20.3	12.6	20.0	35.5	1.0	253.0	108.6	0.67

*Less than detection limit

The highest concentration was of chromium, which reached 421.6 mg/g (Table 9). In the Turkmenbashy Bay the bottom sediments were polluted by nickel (28.5 mg/g), chromium (120.0 mg/g), and barium (501.0 mg/g). Increased concentrations of pollutants were registered close to the places of industrial discharges, as well as in places of dredged bottom material or dumping. The concentration of pollutants in bottom sediments decreased towards the central part of the sea. The only exception is zinc, which occurred in high quantities in the deep part of the basin due to sedimentation of dead plankton organisms.

The pollution of bottom sediments by mercury in the western part of the region, with an average of 0.34 mg/g, was several times higher than in eastern shelf, where it was 0.16 mg/g. The maximum concentrations were fixed in areas near the town of Sumgait (0.78 mg/g), Neftyanye Kamni Bank (0.58 mg/g), in Baku Bight (1.22 mg/g), near Aktau (0.34 mg/g), near Turkmenbashy (0.17 mg/g) and Cheleken (0.23 mg/g) [4].

7 Conclusions

The operation in 1978–2004 of long-term monitoring of the Caspian Sea environmental conditions allowed nominating the main anthropogenic factors of pollution of waters and sediments. River discharge, extraction of oil and gas at the sea shelf, discharge of industrial and municipal wastewaters and garbage, and the dredge and dumping of bottom material are the most important.

The long-term variation and spatial distribution of petroleum hydrocarbons in the waters of the North Caspian clearly indicate a high level of pollution in the 1980s in the estuarine region of the River Ural and on the border with the Dagestan shelf. During the following few years the level of TPHs sharply decreased everywhere down to 0.1–0.2 mg/L. In the last few years a large interannual variation was registered and the main patches of high concentration of petroleum hydrocarbons occurred in the offshore part of the North Caspian rather far from the Volga delta. One can suppose that the Volga was not the main source of TPHs in the North Caspian.

In the shallow waters of the Dagestan shelf the TPH concentration was lower than in the North Caspian and had a clear tendency to decline. The most polluted area was near the town of Izberbash. Recently the estuarine area of the Terek River and the waters near the village of Lopatin were temporary places of high pollution. No vertical stratification in the concentration of petroleum hydrocarbons occurred and all layers were polluted evenly in these shallow waters. The average data from long-term monitoring clearly indicate a weak seasonal dynamic. Slightly increased concentrations characterized the cold season, and some decreasing was visible at the end of summer and in au-

tumn. Very high TPH content in the waters occasionally occurred everywhere and there could be patches of high concentrations due to short-term oil spills or permanent riverine discharge.

Phenol concentration in the North Caspian and Dagestan waters was rather high and showed significant variability both in space and time. On a long time-scale the decrease of phenols in the waters and stabilization during recent years at the level of 0.003–0.004 mg/L were clear. The single highest value occurred in practically every controlled region and in each season. The averaged data smoothed the maximum values and therefore the seasonal variability was not marked. One can observe the local (in space) and short (in time) appearance of patches with high concentrations of phenols.

Detergents in the waters of the North Caspian and at the Dagestan coastal area were present permanently. Their average concentration varied from 0.038 to 0.060 mg/L and has decreased during recent years. The highest values commonly occurred in the western part of the North Caspian and estuarine regions of Dagestan Rivers. The central part of the Middle Caspian was less polluted. The seasonal dynamic described a slight increase at the end of summer, in contrast to the cold period of the year.

Distribution of ammonium concentration was nearly the same as for detergents. High average values were measured in estuarine waters of the Volga, Terek, and Sulak rivers, as well as in the western part of the North Caspian. According to monitoring data there were no interannual and seasonal variations nor vertical gradients.

Among the chlorinated pesticides DDT was the most important in the North Caspian waters in the 1970s and 1980s. The average concentration was 31 ng/L. The common concentration of other pesticides was about 1–2 ng/L. The spatial distribution of pesticides was very unequal and local patches of high concentration usually occurred on a rather clean background. The high values were often measured in the eastern part of the North Caspian. After 1992 the concentration of pesticides of the DDT group was lower than the detection limit used in the analytical methodology.

The spatial distribution of petroleum hydrocarbons in bottom sediments in the North Caspian was not the same as in the water. Zones of high concentrations were measured adjacent to the Volga delta area and on the border with the Dagestan shelf. The sediments in the central part of the region mainly consisted of coarse fractions and were rather clean.

The same features of spatial distribution were described for chlorinated pesticides. Their content was rather high in the 1990s and patches were located in shallow parts close to the Volga delta. Over the last few years the concentration of pesticides has been low and has not often exceeded the detection limit.

The heavy metals in bottom sediments of the North Caspian in general were in the range of regional background values. The patches of high concentration of manganese, nickel, and copper located adjacent to the Volga delta

area were influenced by freshwater inflow. In contrast, the increased levels of iron and zinc were measured in the offshore part of the area far from the delta. Cadmium and lead had rather low concentrations in bottom sediments and were distributed evenly.

In the South Caspian the upper layer of waters were significantly polluted by TPHs, phenols, and detergents. Their concentration slightly decreased from the western shelf towards the east and sharply increased with depth. In the cold season the content of petroleum hydrocarbons in waters was slightly higher. The maximum values were found close to the places of oil and gas extraction on the shelf.

Among pollutants in the bottom sediments of the South Caspian petroleum hydrocarbons were the most important. The western shelf was more polluted than the eastern. The maximum concentrations of TPHs in sediments were measured in the Baku Bight. In general, the highest values occurred in sediments with a fine size spectrum of particles. Long-term dynamics showed stepwise decreasing of TPH pollution in shallow areas. Sediments in the deep part were rather clean.

The concentration of heavy metals in bottom sediments were significantly higher than the regional background level only in vicinity of industrial and municipal waste-water discharge, and in the places of dredge and dumping of bottom sediments. Very high pollution by chromium, mercury, nickel, and strontium was noted in the Baku Bight. In general, the concentration of metals in sediments decreased from the shore to the deep part of the area. Only zinc occurred in high quantity in the deep parts of the basin due to sedimentation of plankton organisms.

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