POLLUTION OF WATER SYSTEMS BY TOXIC CHEMICALS IN THE CONTRACT AREA

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Abstract. *This article brings together the results of analyses of water and sediment samples polluted by organic discharges for assessing the environmental effects of industrial operations in the Contract area. The results of studies indicate the high levels of pollution of surface waters, seawater and marine sediments by toxic hydrocarbons.*

Keywords – pollution seawater wastewater marine sediments phenols

Introduction

Significant development of oil-gas, chemical and petrochemical industries, and subsequent large-scale discharges have resulted in the pollution of air, water and soil components of ecosystem previous studies indicate that there is high concentration of soil contaminants. The degree of contamination varies from 20 to 30% and more. Sometimes, the depth of contamination in soils reaches 2-3 meters. Contaminants accumulated in soils migrated into lakes, reservoirs, surface and ground waters throughout the site. There are over 200 reservoirs of natural and artificial origins, considerable part of which is polluted by oil products. According to [1], more than 2000 ha in Absheron peninsula are occupied by reservoirs contaminated with persistent or non-persistent oily wastes.

Analysing the ecosystem of Absheron peninsula as an integrated, interconnected and interacting system, one should take into account also the impact of environmental pollution on the Caspian ecosystem. Extensive environmental studies create a sound scientific basis for assessing environmental situation in the Caspian region [2].

The subject of this study was to determine the pollution of surface water, seawater and bottom sediments by organic wastes.

Materials and methods

Over 70 samples of surface water, marine sediments and seawater were analysed during the studies.

The seawater and marine sediments used were sampled in the Caspian Sea, in offshore shelf of the Contract area. Surface water samples were taken from the sites adjacent to this area. The data considered here are limited to 15 sampling points comprised of 10 onshore and 5 offshore stations located throughout the study area. Stations 11, 12 and 13 were at distances of 5, 3 and 2 km from seacoast, respectively. Stations 14 and 15 were located within relatively shallow water sections.

Sampling was performed at 4-5 m/s wind speed according to general guiding principles [3, 4]. Seawater and sediment samples were collected from two depth of each station in a vessel, using bathometer and grabs. Surface waters were sampled in 10 stations on the study site. The samples were maintained in refrigerators at - 4 ± 2°C.

The following chemicals were analysed in water and sediment samples:

1. **Total petroleum hydrocarbons (TPH)** – total petroleum hydrocarbons - aliphatic, alicyclic and aromatic hydrocarbons- were analysed by gas chromatography method (Hewlett Packard GC HP 6890, limit of detection & range – 10 mg/l & 10 ng/l));
2. **Polyaromatic hydrocarbons (PAHs)** – USEPA 16 PAHs and 2-6 rings PAHs were analysed gas chromatography –mass spectroscopy method (Hewlett Packard GC-MS 5973, limit of detection & range – 10 mg/l & 10 ng/l);
3. **Phenols** – total concentration of phenols including ortho- and meta-phenols substituted with halogens, carboxyl, methoxyl and sulphanole groups was analysed by spectrophotometric method (CECIL 4004 spectrophotometer, limit of detection & range - 0.5 mg/l – 100 mg/l);
4. **Surface active agents (SAA)** - SAA were analysed by spectrophotometric method (CECIL 4004 spectrophotometer, limit of detection & range - 0.5 mg/l – 100 mg/l).

Results

The laboratory measurements revealed the presence of a large number of different organic chemicals in water and sediment samples. In surface water, for example, TPH, 2-6 rings PAHs, NPHD (total naphthalene, phenanthrene and dibenzothiophene) and UCM (undecomposable complex mixture of hydrocarbons) each had highest concentrations (Table 1). In addition, measurable levels of USEPA 16 PAHs and SAA were also found in several samples (Stations 2,3,5,8, 9 and 10) of surface water.

Table 1. Concentration of hydrocarbons in surface water samples

Samp. Station	**Concentration, mkg/l**								SAA, mg/l
	TPH	TPH,%	2-6 rings PAHs	USEPA 16 PAHs	NPHD[1]	NPHD, %	Phenols	UCM[2]	
1	128.5	74.2	1.45	0.10	1.30	90.0	0.09	95.4	0.47
2	53580	75.4	1096	36.56	1019	93.0	0.83	40422	9.64
3	6023	82.9	98.9	3.12	89.17	90.0	0.40	4990	7.68
4	1796	92.4	4.8	0.86	0.74	15.0	0.06	1659	0.34
5	4756	85.7	176	3.18	166.4	95.0	1.40	4078	1.47
6	20.9	8.1	0.41	0.07	0.28	69.0	0.63	1.7	0.41
7	68.2	35.6	0.42	0.05	0.35	83.0	0.79	24.3	0.20
8	5749	87.5	184.9	4.91	166.4	90.0	0.94	5030	1.21
9	1890	79.9	62.1	3.53	53.7	87.0	<0.05	1511	8.39
10	333.1	11.3	21.7	1.50	21.0	97.0	0.59	37.5	8.70
MAC	0.05						0.001		0.2-0.5

NPHD[1]- total naphthalene, phenanthrene and dibenzo-thiophene

UCM[2]- undecomposable complex mixture of hydrocarbons (including cycloalkanes)

All USEPA 16 PAHs were present in wastewater samples. Concentrations of naphthalene, fluorene, phenanthrene, pyrene, fluoranthene, chryzene and benzopyrene varied from 1.3 to 20690.6 ng/l (Table 2).

Table 2. Content of USEPA 16 PAHs in wastewater samples (ng/l)

USEPA 16 PAHs	Sampling stations				
	1	2	3	4	5
1.Naphthalene	27.8	1056.4	47.4	21.7	49.3
2.Acenaphthylene	0.7	120.9	131.2	14.0	20.4
3. Acenaphtene	2.2	246.4	33.4	5.2	54.8
4. Fluorene	8.5	4134.7	215.7	5.5	1208.6
5. Phenanthrene	20.4	20690.6	1376.5	25.0	532.3
6. Anthracene	1.7	564.9	45.7	9.3	75.1
7. Fluoranthene	3.4	723.5	79.6	18.0	83.3
8. Pyrene	7.5	1368.9	194.4	171.7	240.2
9. Benzo(a) anthracene	1.2	761.7	44.4	17.8	102.4
10. Chryzene	13.9	5121.1	753.5	195.4	669.5
11.Benzo(b)fluoranthene	3.6	470.1	70.2	29.8	53.0
12.Benzo(k)fluoranthene	1.5	344.0	36.4	16.2	17.9
13.Benzo(a)pyrene	1.3	348.2	39.3	74.5	22.3
MAC of benzopyrene-5	**-**	***69***	***8***	***15***	***4.5***
14.Indeno(1,2,3 cd)pyrene	3.6	121.5	8.9	97.3	5.3
15.Benzo(ghi)perilene	4.3	301.4	28.8	139.7	26.8
16. Dibenzo(ah)anthracene	0.7	188.5	13.0	22.9	14.6
TOTAL	**102.3**	**36562.8**	**3118.4**	**864.0**	**3175.8** Continued

Table 2 (continued). Content of USEPA 16 PAHs in wastewater samples (ng/l)

USEPA 16 PAHs	Sampling stations				
	6	7	8	9	10
1.Naphthalene	14.4	15.5	47.3	608.3	580.0
2.Acenaphthylene	0.4	0.7	22.9	15.2	5.1
3. Acenaphtene	0.8	0.8	100.3	99.9	46.8
4. Fluorene	1.4	3.3	785.5	263.4	147.2

5. Phenanthrene	7.2	10.4	1827.9	1235.9	454.3
6. Anthracene	1.0	0.3	84.1	132.0	14.8
7. Fluoranthene	6.4	3.1	103.7	47.1	16.0
8. Pyrene	8.5	6.3	329.9	336.7	89.4
9. Benzo(a) anthracene	3.5	0.3	173.2	75.2	4.5
10. Chryzene	8.7	1.9	1122.5	476.4	122.4
11.Benzo(b)fluoranthene	3.8	0.7	105.0	51.6	5.3
12.Benzo(k)fluoranthene	2.2	1.1	54.6	24.6	4.5
13.Benzo(a)pyrene	2.9	2.3	68.4	58.0	2.7
MAC of benzopyrene-5	**-**	**-**	***13.6***	***11.6***	**-**
14.Indeno(1,2,3 cd)pyrene	3.4	0.5	14.5	23.8	0.0
15.Benzo(ghi)perilene	3.5	2.0	42.6	67.1	6.0
17. Dibenzo(ah)anthracene	0.9	0.0	29.4	13.9	0.0
TOTAL	**69.0**	**49.2**	**4911.8**	**3529.1**	**1499.0**

Comparative analysis of hydrocarbon content in seawater and marine sediments (Table 3) shows that concentrations of TPH in all samples exceed MAC by 3 to 20 times. The content of TPH in marine sediments at Stations 11 and 12 is considerably higher than the content of those in seawater samples. These stations are exposure to wastewater flowing from a discharge channel. In the samples taken from Stations 13 and 15 seawater contain more TPH than marine sediments, although Station 15 is directly exposed by the above mentioned cannel. Stations 11 and 15 are located at different distances from seacoast. According to Table 3, the content of hydrocarbons in seawater samples considerably decreases depending on the remoteness of stations from seacoast, whereas, significantly increased levels were detected in sediments even at 5 km from the coast. This indicate that exposure to discharge channel has greatly contributed to the pollution of a large area by oil products within the study site. The level of pollution extended up to 5 km offshore. Relatively lower pollution levels are detected at Station 13. The results have shown that the degree of pollution at this station exceeds the MAC only about 3 times.

Table 3. Hydrocarbon concentration in seawater and marine sediments

Sampling Stations		**Concentration, mkg/l**						
		TPH	TPH, %	2-6 rings PAHs	USEPA 16 PAHs	NPHD	NPHD, %	UCM
11	Water	155.1	87.8	0.22	0.03	0.19	84.0	136.1
	Sediment (depth–5 m)	1140	-	4.3	1.2	1.0	24.0	1060
12	Water	148.0	86.2	0.27	0.03	0.24	88.0	127.5
	Sediment (depth-4.5 m)	1197	-	7.2	0.9	2.9	41.0	1096
13	Water	154.1	93.1	0.21	0.03	0.16	75.0	143.5
	Sediment (depth-6m)	128.8	-	0.6	0.1	0.5	72.0	113.6
14	Water	2041	89.9	7.14	0.32	5.11	72.0	1836
	Sediment (depth–2.3 m)	246.7	-	5.1	0.2	4.3	84.0	227.1
15	Water	1340	91.4	4.90	0.20	3.85	79.0	1225
	Sediment (depth- 1.5m)	1230	-	19.7	0.40	17.4	88.0	1128
****MAC(oil and oil prod.)***		***0.05 mg/l***						

*MAC for fishery standards

As can be seen from Tables 4 and 5, USEPA 16 PAHs in all sediment samples are detected at significantly increased levels, compared to the samples taken from upper horizons of the same stations (with exception of Station 14). Concentration of USEPA 16 PAHs in marine sediments at Stations 11 and 12 is 19 and 27 times higher than the concentration of those in water samples. This is the evidence of long-term accumulation of high carcinogenic compounds in marine sediments due to the migration of wastewater into deep sections. It is clear that decomposition of these compounds in this condition proceeds very slowly [5].

Table 4. Concentration of USEPA 16 PAHs in seawater samples (ng/l)

USEPA 16 PAHs	**Sampling stations**				
	11	12	13	14	15
1.Naphthalene	4.6	4.4	5.1	6.3	8.6
2.Acenaphthylene	2.8	2.1	4.5	9.6	7.4
3. Acenaphtene	0.5	0.4	0.7	6.6	3.3
4. Fluorene	0.7	0.7	1.2	13.6	14.4
5. Phenanthrene	5.8	2.1	2.9	18.2	19.8
6. Anthracene	2.2	2.0	1.1	9.9	7.1
7. Fluoranthene	0.7	11.4	0.9	7.4	5.5
8. Pyrene	1.6	1.9	2.2	56.4	24.8
9. Benzo(a) anthracene	0.4	0.8	0.8	13.8	5.1
10. Chryzene	3.7	3.4	3.6	110.2	76.7
11.Benzo(b)fluoranthene	0.5	0.5	0.6	15.7	9.2
12.Benzo(k)fluoranthene	0.3	0.3	0.5	5.4	3.3
13.Benzo(a)pyrene ***Exceeding MAC***	0.1 -	0.3 -	0.3 -	8.4 ***1.7 times***	4.7 -
14.Indeno(1,2,3 cd)pyrene	0.4	0.6	0.7	9.2	5.1
15.Benzo(ghi)perilene	1.2	0.9	1.6	22.4	6.5
18. Dibenzo(ah)anthracene	0.7	0.3	0.2	6.6	2.0
TOTAL	**26.2**	**32.1**	**26.9**	**319.7**	**203.5**

Table 5. Concentration of USEPA 16 PAHs in marine sediment samples (ng/g)

USEPA 16 PAHs	**Sampling stations**				
	11 (5 m deep)	12 (4.5m deep)	13 (6 m deep)	14 (2.3 m deep)	5 (1.5 m deep)
1.Naphthalene	131.7	24.4	1.9	5.7	7.6
2.Acenaphthylene	2.5	5.4	0.1	0.9	4.8
3. Acenaphtene	21.8	5.9	0.4	3.9	9.3
4. Fluorene	18.7	7.0	1.5	22.3	73.3
5. Phenanthrene	187.7	156.2	9.1	42.3	76.9
6. Anthracene	31.8	42.4	1.1	7.6	8.2
7. Fluoranthene	125.1	36.2	2.2	9.6	10.0
8. Pyrene	112.9	69.3	2.9	27.2	47.9
9. Benzo(a) anthracene	76.4	46.1	1.0	12.0	16.3
10. Chryzene	102.8	104.2	21.7	40.7	122.8
11.Benzo(b)fluoranthene	99.5	84.8	2.9	13.4	15.4
12.Benzo(k)fluoranthene	55.4	36.0	1.3	6.0	6.3
13.Benzo(a)pyrene ***Exceeding MAC***	80.9 ***16.2 times***	60.9 ***12 times***	1.6 -	9.4 ***1.9 times***	5.2 -
14.Indeno(1,2,3 cd) pyrene	75.2	79.6	2.0	9.5	8.5
15.Benzo(ghi)perilene	90.4	107.8	3.9	12.1	20.7
19. Dibenzo(ah) Anthracene	34.9	44.0	1.0	4.0	5.6
TOTAL	**1247.7**	**910.2**	**54.6**	**226.6**	**438.8**

In order to provide information about the level of pollution of water systems in the Contract area by organic chemicals and their potential impact on the quality of the Caspian water, the MAC of several toxic compounds in wastewater are shown in Table 6.

Table 6. MAC of pollutants in wastewater falling into reservoirs

Pollutants	**MAC for reservoirs, mg/l**	
	Sanitary water quality standards	Fishery water quality standards
Oil and oil products	0.1 – 0.3	0.05
Surface active agents	0.4 – 0.5	0.2 – 0.5
Phenol	0.001	0.001
Naphthalene	0.05	0.004
Benzopyrene	0.000005	0.000005

Results indicate that the concentration of oil products in all samples, with the exception of samples from Station 7 (Absheron main channel) and Station 6 (the end of solid waste disposal site), exceeds the MAC by tens orders of magnitude. Significantly increased levels were detected in oil polluted water discharges (Stations 2 and 3). The highest level of pollution occurred at the flow within the territory of Contract area. The data derived from surface water analyses (Table 1) show that discharges of iodine factory (Station 5) are heavily polluted by TPHs (4.7 mg/l). In a word, concentration of TPHs in all samples at coastal locations of the study area (1.55-2.0 mg/l) exceed the MAC by several times. This is the evidence of pollution of sea aquatory due to the migration of wastewater into the sea.

In over 66% of surface water samples including relatively shallow waters of coastal area, concentration of PAHs (naphthalene and banzopyrene, especially) exceeded the MAC by several times. However, no exceeding of MAC on PAHs was observed at the locations of Absheron main channel and solid waste disposal site (Stations 6 and 7) and also at Stations 1,2, and 3.

Detectable concentrations of USEPA 16 PAHs were found in all samples. It is known that all of the USEPA 16 PAHs fall into the category of “high carcinogenic organic chemicals” in the system of classification of chemicals’ toxicity.

Significantly increased levels of the most carcinogenic compound - benzo(a)pyrene -348.2 ng/l were detected at three waste water discharge locations (Stations 2, 8 and 9) and also in oil polluted lake -58.0 to 68.4 ng/l (Station1). In most polluted points, the concentration of benzo(a)pyrene exceeded the MAC by several orders of magnitude. Similar tendency was also observed for other 15 PAHs such as phenanthrene, anthracene, fluoranthene and etc.

Concentrations of PAHs were detected at relatively high levels in samples taken from shallow water locations (Stations 14 and 15), compared to other coastal areas.

Analyses have shown that the concentration of phenols exceeded the MAC in all samples at both onshore and offshore locations of the study site. Even in samples from Absheron main channel (Station 7), where the contents of TPH and PAH don’t exceed the MAC, the concentration of phenols exceed the MAC by 8 times.

The SAA often found in reservoirs due to chemical industry’s discharge are very dangerous because of their persistence and undecomposability under microorganisms’ exposure conditions.

The results of analyses indicate that a group of surface water samples contain increased amount of anionic SAA (Table 1) exceeding the MAC to some extent depending on sampling location. So, in samples from two distinct locations (Stations 2 and 3) of wastewater discharge channel, one of which situated on the entrance of the Contract area (Station 3), concentration of SAA exceeded the MAC by 19 and 15 times, respectively. This is the evidence of the fact that flowing through the Contract area water is polluted by an additional amount of SAA. The content of SAA not exceeded the MAC only at Station 7 and relatively clean surface waters. However, concentrations of SAA exceeded the MAC from 16 to 32% even at 2-5 km offshore locations. This indicate that considerable amount of SAA is carried to the Caspian Sea and the self-purification capability of water from this toxicants is very low [5,6].

Conclusions

Based on the results of studies on the pollution of Contract area, it has generally been concluded that:

1. All samples of wastewater discharged to the coastal area were heavily polluted by hydrocarbons. The results in all cases are quite similar, showing high concentrations of TPHs, PAHs, USEPA 16 PAHs and phenols. Significantly increased levels of pollution are detected in samples taken from oil

polluted discharge channel and in wastewater of iodine factory (Stations 2 and 5).

2. The highest levels of pollution occur at wastewater flow in the Contract area. This is the evidence of the fact that waters were polluted by additional amount of hydrocarbons when passed the Contract area.

3. The quality of surface waters of the Contract area does not meet the established water quality standards. A huge amount of pollutants is carried to the sea by surface waters.

4. Most of surface water, seawater and sediment samples contain considerable amount of carcinogenic USEPA PAHs including benzo(a) pyrene, chryzene, phenanthrene and etc. The content of PAHs in 66% of water samples exceeds is the MAC by several times.

5. Concentrations of TPH in seawater and sediment samples exceed the MAC from 3 to 20 times. Sometimes, in samples taken from the same stations (11 and 12) marine sediments contained more TPH than seawater. These sampling stations are exposure to the wastewater flowing from a discharge channel. Significantly increased levels of pollution were detected in sediments even at 5 km offshore location. The measurements confirm that exposure to discharge channel has greatly contributed to the pollution of a large area by oil products within the study site.

6. Major part of surface water samples contain increased amount of anionic SAA The concentration of SAA in several samples exceeded the MAC 15 to 19 times. Besides, pollution of waters by SAA was observed even at 2-5 km offshore locations exceeding the MAC 16 to 32%. These data indicate that considerable amount of SAA is carried to the Caspian Sea and self-purification capability of water from this toxicants is very low.

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КОНТРАКТ САЩЯСИНДЯ СУ СИСТЕМЛЯРИНИН ЗЯРЯРЛИ КИМЙЯВИ МАДДЯЛЯРЛЯ ЧИРКЛЯНМЯСИ

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Мягалядя нефт сянайесиндя апарылан ишлярин Контракт сащясиндя ятраф мщщитя тясирини мцяййян етмяк цчцн су вя диб чюкцнтцляри нцмунялярининин анализинин нятиъяляри верилмишдир. Тядгигатын нятиъяляри йерцстц су щювзяляринин, дяниз суйунун вя диб чюкцнтцляринин мцхтялиф зярярли карбощидроэенлярля йцксяк дяряъядя чирклядийини эюстярир.

ЗАГРЯЗНЕНИЕ ВОДНЫХ СИСТЕМ НА КОНТРАКТНОЙ ПЛОЩАДИ ТОКСИЧНЫМИ ХИМИКАТАМИ

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В статье рассматриваются результаты анализов проб воды и донных отложений, загрязненных органическими веществами с целью определения воздействия промышленных операций на окружающую среду контрактной площади. Результаты исследований показывают высокую степень загрязненности поверхностных водоемов, морской воды и донных отложений разными токсичными углеводородами.