POLLUTION LEVEL OF OIL INDUSTRIAL WATER SAMPLES

E. Gadirova [1]

[1]Baku State University, Baku, Azerbaijan

elmina2010@mail.ru

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Organic toxic compounds such as polycyclic aromatic hydrocarbons, phenolic compounds are a global environmental concern as they cause inflammation and skin cancer. As you know there are two types of anthropogenic sources of hydrocarbons: petrogenic and pyrogenic sources. Petrogenic sources include crude oil and petroleum-derived hydrocarbon compounds. Pyrogenic sources of hydrocarbon compounds are formed as a result of incomplete combustion of organic substances such as oil, wood, coal. Before entering the open sea these oil products pass through the entire coastal zone. It is known that industrial waters are discharged into reservoirs after various chemical processes. The aim of this work was to determine how dangerous industrial oil water is when it enters the aquatic ecosystem. The article investigates the chemical composition of wastewater from the oil industry and identifies organic toxic compounds - polycyclic aromatic hydrocarbons and phenolic compounds. At the same time, the amount of heavy metals in water samples was analyzed. For chemical analysis, 3 samples were taken from the territory of the refinery. In total, 15 polycyclic aromatic hydrocarbons, 13 phenolic compounds and 9 heavy metals were analyzed in water samples. Water samples were analyzed in accordance with the contract HS-153/2-18 between Heydar Aliyev Oil Refinery and Baku State University's Department of Ecological Chemistry. The chemical analyses of heavy metals, polycyclic aromatic hydrocarbons and phenolic compounds were carried out using extremely sensitive devices such as Perkin Elmer ICP/OES-2100DV and GC-MSD gas chromatograph 6890N with a highly efficient mass-selective detector-Agilent 5975. In the Khazar Ecological Laboratory performed quantitative analysis of organic compounds in water samples as well as heavy metal determination.

Keywords: *heavy metals, industrial water, polycyclic aromatic hydrocarbons, phenol, water pollution*

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1. Introduction

Organic compounds such as polycyclic aromatic hydrocarbons (PAHs) are a global environmental concern as they cause inflammation and skin cancer. As you know there are two types of anthropogenic sources of hydrocarbons: petrogenic and pyrogenic sources.

Petrogenic sources include crude oil and petroleum-derived hydrocarbon compounds. Pyrogenic sources of hydrocarbon compounds are formed as a result of incomplete combustion of organic substances such as oil, wood, coal.

About 6.1 million tons of oil products are thrown into the ocean annually most of which are of anthropogenic origin. It is known from the literature that according to the latest indicators every year 6 mln tons of oil and oil products are discharged to the world ocean. Pyrogen and petrogen pollution of sea water contamination with ballast water and so on causes pollution of common water basins. These hydrosphere segments are a dynamic system which leads to a decrease and depletion of fresh water supplies over time [1,2].

There are many ways to treat wastewater. Since these treatment methods are not completely effective therefore they become a serious threat to the flora and fauna of the Caspian Sea. We know that after treatment wastewater from the oil refining industry is discharged into the Caspian Sea. Wastewater from the oil industry negatively affects the biota of the sea.

The Caspian Sea is a very sensitive ecosystem. Over the past decades under the influence of anthropogenic and biochemical factors the state of ecosystems in general has deteriorated sharply and especially in the northeastern part of the sea [3]. Observations of recent years show that the waters of the Caspian Sea especially along the coast of the National Park are also polluted by oil and sewage [4].

Industrialization and urbanization in the Caspian region has developed rapidly over the past several decades and the associated increase in hydrocarbons is a concern in the region. Offshore production and accidental oil spills, industrial waste, wastewater, discharges flowing down from river water are considered the main source of anthropogenic hydrocarbons in the marine environment [5].

Industry is believed to be the main source of oil pollution in the Caspian Sea [6]. The total amount of industrial waste discharged into the Caspian Sea averages 2342.0 million m^3 per year. Such waters contain 122.5 thousand tons of oil, 1.1 thousand tons of phenols, 9.9 thousand tons of organic chemistry products.

The total content of hydrocarbons in the North-Western part of the South Caspian was small - 32-54.2 μg/g. In this area in the vicinity of oil fields the concentration of phenol was 0.002-0.003 μg/g [7,8]. Pollution of water and bottom sediments is noted throughout the Absheron Peninsula and in the Baku Bay. The main volume of pollution (90% of the total) enters the Caspian Sea with river runoff. After purification these waste waters are discharged into the Caspian Sea and even in small quantities these harmful substances are dangerous for the flora and fauna of the sea and the environment.

As is already known PAHs are very dangerous for the environment for living organisms in aquatic ecosystems and therefore the identification of hazardous substances and the application of methods for their destruction is very important [9,10].

2. Materials and Methods

The quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) also of phenol and its derivatives were carried out in a system including an Agilent 6890N gas chromatograph which has an interface with an Agilent 5975 high-performance mass-selective detector manufactured by Agilent Technologies (USA).

The chromatograph was equipped with a splitless injector and a ZB-5 capillary column (Phenomenex, USA). Column ZB-5 has the following specifications: 5 %-biphenyl 95 %-dimethylpolysiloxane copolymer length-60 m inner diameter 0.25 mm film thickness 0.25 μm. Helium (99.999 % purity) with a flow rate of 1.5 ml/min was used as a carrier gas. The temperature rise was programmed from 40 °C to 310 °C. The extracts were introduced using an automatic sampler in a volume of 1 μl (Dettmer-Wilde, 2014).

Quantitative analysis was performed against a seven-point calibration against standard reference solutions. A mixture of deuterated polycyclic aromatic hydrocarbons: naphthalene-d8, phenanthrene-d10 (Cambridge Isotope Laboratories, Inc., Andover USA) was used as an internal standard for calculating the obtained results of chromatographic analysis [11].

3. Results and Discussion

At first PAHs were analyzed in water samples discharged from the oil industry into the Caspian Sea. The results of the analyses and chromatograms for each sample are given below (Table1 1).

Table 1. *Determination of polycyclic aromatic hydrocarbons in water samples taken from the Oil Refinery*

PAH, mg/l	Standard indicator	1 sample	2 sample	3 sample
Naphthalene	≥0.01	0.08	0.23	20
Achenthylene	≥0.01	0.02	0.51	15
Acenaften	≥0.01	0.04	0.33	43
Fluoren	≥0.01	0.24	0.81	80
Fenantren	≥0.01	0.29	4.32	298
Anthracene	≥0.01	0.04	0.33	26
Fluoranten	≥0.01	0.03	3.01	15
Piren	≥0.01	0.05	13	66
Benz (a) anthracene	≥0.01	0.01	3.5	17
Chrezen	≥0.01	0.02	15	41
Benz (b + j + k) fluorantene	≥0.01	<0.01	2.2	5.0
Benz (a) pyrene	≥0.01	<0.01	1.3	5.0
Inden (1,2,3-cd) pyrene	≥0.01	<0.01	0.37	1.5
Benz (ghi) perilen	≥0.01	<0.01	0.63	1.7
Dibenz (ah) antracen	≥0.01	<0.01	0.57	1.8

It should be noted that excess PAHs are expected to be present in refinery wastewater. Wastewater of this type is biologically treated and then discharged into the Caspian Sea.

Figures 1-3 demonstrate the chromatograms taken for 3 water samples of the oil industry.

Phenol and its derivatives were also determined in the water samples of the oil industry and the results are given in Table 2.

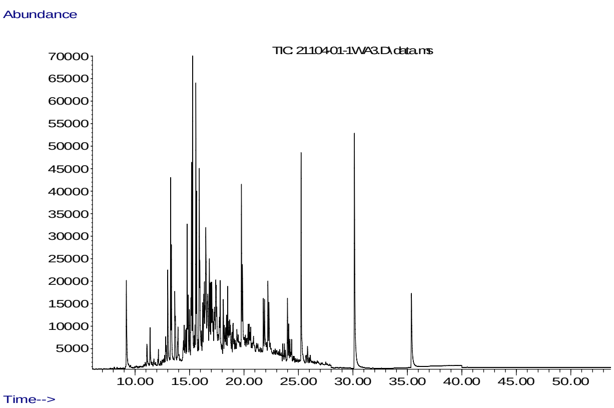

Fig. 1. *GC-MSD spectroscopy of sample 1*

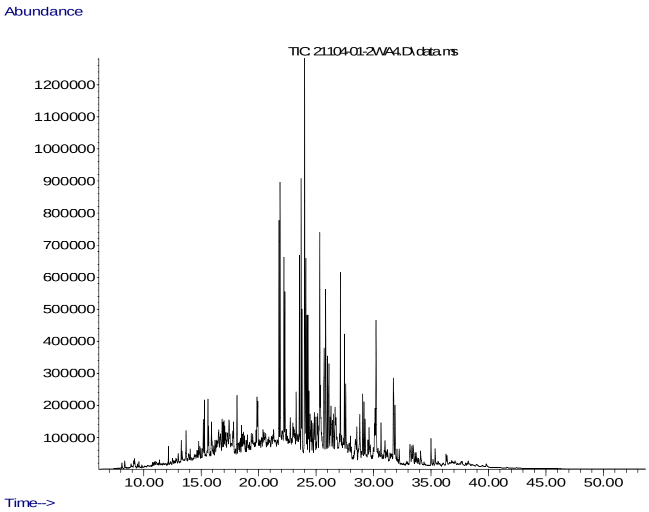

Fig. 2. GC-MSD spectroscopy of sample 2

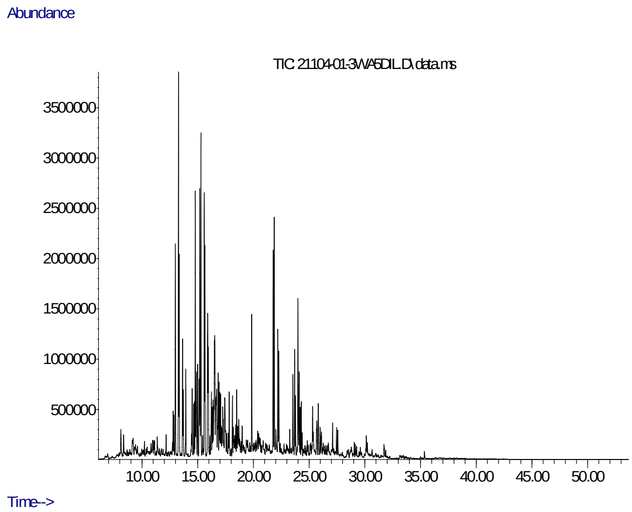

Fig. 3. GC-MSD spectroscopy of sample 3

Table 2. *Determination of phenol and its derivatives in water samples taken from the Oil Refinery*

Compounds, mg/l	Standard indicator	1 sample	2 sample	3 sample
phenol	≥0.04	5.34	5.65	1.44
o-cresol	≥0.04	0.76	0.26	0.16
2-nitrophenol	≥0.04	0.59	0.48	0.08
2,4-dimethylphenol	≥0.04	31.99	8.71	0.20
m,p-cresol	≥0.04	20.59	3.81	0.85
2,6-dichlorphenol	≥0.04	1.14	0.67	1.80
4-chloro-3-methylphenol	≥0.04	0.63	0.43	0.69
2,4,5-TCP	≥0.04	0.48	0.28	0.18
2,4,6-TCP	≥0.04	0.14	0.04	0.25
2,3,4,6-tetrachlorophenol	≥0.04	0.27	0.18	0.002
2-methyl-4,6-dinitrophenol	≥0.04	<0.04	<0.04	<0.04
pentachlorphenol	≥0.04	0.27	0.25	0.06
2-sec-butyl-4.6-dinitrophenol	≥0.04	<0.08	<0.08	<0.08

The high amount of phenol in the 2 water sample is due to sampling from a water tank located closer to the production site.

At the same time heavy metal ions were identified in the water samples examined. Heavy metals enter aquatic living organisms and enter the human body through the food chain.

Determination of heavy metals was performed by ICP-OES, Optima 2100DV emission analysis method.The results are shown in the Table 3.

Table 3. *Amount of heavy metals in wastewater samples of the Oil Refinery*

Heavy metals, mg/l	1 sample	2 sample	3 sample
Fe	0.048	0.047	0.042
Zn	0.143	0.078	0.023
Cu	0.023	0.028	0.020
Mn	0.021	0.105	0.038
Pb	0.022	0.017	0.009
Cd	0.007	0.006	0.008
Cr	0.004	0.003	0.004
Co	0.009	0.014	0.012
Ag	0.009	0.010	0.008

All these metals are dangerous if they exceed the MPC norm, but Cd is more dangerous. Norm for Cd is 0.001 mg/l (mg/dm^3). As can be seen from the table the amount of Cd in the studied samples is higher than the norm.

Even after purification these values remain high since phenol and its derivatives are highly soluble in water and difficult to remove from water. It should be noted that chlorinated phenol derivatives in the aquatic ecosystem are 150-200 times more toxic than phenol itself. As can be seen from Table 2 the values of phenol and its derivatives were higher in the water samples 1 and 2. In the third sample the amount of phenol was less than in the samples 1 and 2 [12].

After treatment industrial wastewater is discharged into the Caspian Sea and it is very important to purify the water in accordance with the norm since the flora and fauna of the aquatic ecosystem is disturbed. As a rule wastewater from the oil industry is rich in toxic substances of organic origin depending on the processes taking place on them.

Therefore the amount of PAHs, heavy metals also phenol and phenolic organic compounds in water samples are often higher than normal.

4. Conclusions

It is known that the waste water of the oil industry is very dangerous for the aquatic ecosystem. Thus, it causes serious damage to flora and fauna of water ecosystem. For this purpose, 3 waste water samples were taken from the oil industry and analyzed. The goal was to determine their composition. For this purpose, PAHs, phenolic organic compounds and heavy metals were determined in water samples.

Chemical analysis of water samples were carried out on a GC-MSD gas chromatograph 6890N with a highly efficient mass-selective detecto-Agilent 5975.In water samples heavy metals were analyzed on a PerkinElmer ICP/OES-2100DV.A total of 15 PAHs, 13 phenolic and heavy metals compounds were analyzed in water samples. As in the analysis of PAHs the most dangerous naphthalene were observed in the water samples 2 and 3. The MPC limit for PAHs is 0.01 mg/l. Naphthalene belongs to a class of high-risk substances and is considered the most hazardous among PAHs. Therefore, the main focus was on which areas of the water samples had the highest levels of naphthalene. The amount of phenol was higher in water samples 1 and 2.

In general, the permissible concentration of phenol for industrial water in the maximum case should be 0.1 mg/l. In this 3, 1, 2 samples the amount of phenol gradually increases: 1.44–5.34–5.65 mg/l. As for heavy metals most of them (mainly Cd) have exceeded the limit.

References

1. Hajiyeva, S. R.; Gadirova, E. M. Methods for cleaning water contaminated with oil. *Azerbaijan Chemistry Journal* **2014**, *1*, 35–38. https://doi.org/10.32737/0005-2531

2. Hajiyeva, S. R.; Gadirova, E. M. Monitoring of the petro-genically polluted territories E3S *Web of Conferences ICBTE*, 2020. https://doi.org/10.1051/e3sconf/202021201006

3. Caspian Sea.State of the Environment. Report of the Interim Secretariat of the Framework Convention for the Protection of the Marine Environment of the Caspian Sea and the Bureau for Management and Coordination of the CASPECO Project, 2011.

4. Kostianoy, E. A.; Kosarev, A.; Korshenko, A.; Gul, A. G. The Caspian Sea Environment Water Pollution. Pollution of the Caspian Sea. *Hdb. Env. Chem* **2005**, *5*, 109–142.

5. Novikov, Yu. V. *Ecology of the environment and man*; Moscow, 2005.

6. Ostroumov, S. A. Problems of ecological safety of water supply sources. *Hdb. Env. Chem* **2006**, *5*, 17–20.

7. Neff, J. M. *Bioaccumulation in marine organisms*; Elsevier: Amsterdam, 2002.

8. Yunker, M. B.; Macdonald, R. W.; Vingarzan, R. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* **2002**, *33*, 489–515.

9. Opekunov, A. Yu.; Kholmyanskiy, M. A.; Kurylenko, V. V. *Introduction to the ecogeology of the shelf*; Publishing house of St. Petersburg University: St. Petersburg, 2000.

10. Kostianoy, E. A.; Kosarev, A.; Korshenko, A.; Gul, A. G. The Caspian Sea Environment Water Pollution. Pollution of the Caspian Sea. *Hdb. Env. Chem* **2005**, *5*, 109–142.

11. Dettmer-Wilde, K.; Engewald, W. *Practical Gas Chromatography. A Comprehensive Reference*; Springer-Verlag: Berlin, 2014. http://doi.org/10.1007/978-3-642-54640-2

12. Hajiyeva, S. R.; Gadirova, E. M. Determination of phenol and its derivatives contained in wastewater after the catalytic cracking process. *Advances in Biology & Earth Sciences* **2018**, *3*(3), 248–256.

РІВЕНЬ ЗАБРУДНЕННЯ У ПРОБАХ ВОДИ НАФТОВОЇ ПРОМИСЛОВОСТІ

Гадірова Е.[1]

[1]Бакинський державний університет, Баку, Азербайджан

elmina2010@mail.ru

Органічні токсичні сполуки, такі як поліциклічні ароматичні вуглеводні та фенольні сполуки є глобальною екологічною проблемою, оскільки вони викликають запальні процеси та рак шкіри. Як відомо, антропогенні джерела вуглеводнів бувають двох типів: петрогенні та пірогенні. До петрогенних джерел відносяться сира нафта та отримані з нафти вуглеводневі сполуки. Пірогенне утворення вуглеводневих сполук відбувається в результаті неповного згоряння органічних речовин, таких як нафта, деревина, вугілля. Перед потраплянням у відкрите море ці нафтопродукти проходять через всю прибережну зону. Відомо, що промислові води скидаються у водойми після різних хімічних процесів. Метою цієї роботи було визначити, наскільки небезпечними є води нафтової промисловості для водних екосистем. У статті досліджено хімічний склад стічних вод нафтової промисловості та визначено вміст органічних токсичних сполук – поліциклічних ароматичних вуглеводнів та фенольних сполук. Також у пробах води досліджено вміст важких металів. Для хімічного аналізу було відібрано три проби з території нафтопереробного заводу. Загалом у пробах води визначено 15 поліциклічних ароматичних вуглеводнів, 13 фенольних сполук та 9 важких металів. Проби води аналізували відповідно до контракту HS-153/2-18 між нафтопереробним заводом імені Гейдара Алієва та кафедрою екологічної хімії Бакинського державного університету. Хімічний аналіз важких металів, поліциклічних ароматичних вуглеводнів і фенольних сполук проводився з використанням надзвичайно чутливих пристроїв, таких як Perkin Elmer ICP/OES-2100DV та газовий хроматограф GC-MSD 6890N з високоефективним мас-селективним детектором Agilent 5975. Кількісний аналіз органічних сполук у пробах води, а також визначення важких металів було здійснено у Хазарській екологічній лабораторії.

Ключові слова: *важкі метали, забруднення води, поліциклічні ароматичні вуглеводні, промислові води, фенол*