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## LEVEL OF ORGANIC TOXIC COMPOUNDS IN AQUATIC ECOSYSTEMS

**Monitoring of water samples taken from some territories was carried out. So that water samples were taken from 7 different regions of the Caspian Sea and analyzed for mainly toxic organic compounds – PAHs, phenol, and its derivatives. The analyses were carried out using extremely sensitive devices such as GC-MSD gas chromatograph 6890N with a highly efficient mass-selective detector-Agilent 5975. It was determined that the investigated toxic organic compounds in the wastewaters of the Caspian Sea coast exceed the permissible limit. This fact was formed against the background of serious negative impacts on the flora and fauna of the Caspian Sea with the discharge of industrial wastewater. In water samples, 15 PAHs and 11 phenolic compounds were analyzed.**

***Keywords*: monitoring; phenol; PAH; the Caspian Sea; aquatic system; analyses.**

**Introduction:**

Wastewater from the chemical industry and petrochemical enterprises is considered more dangerous for the environment. According to experts from the United Nations (UN) 100,000 out of one million products produced in the world are chemical compounds. Most of these compounds (15,000) are carcinogens to the environment, especially to humans. Biochemical decomposition of these compounds which are not analogous in nature and are distributed in water bodies, is not possible. 80% of the chemical compounds released into the atmosphere enter water bodies after a certain period of time. It should be noted that the role of various types of waste released into the atmosphere in the pollution of water bodies is great. Atmospheric pollutants are spread over long distances by air currents and then enter groundwater and surface water through rainwater. Thus the degree of pollution of the aquatic environment is higher than that of the soil and air (Garib Mammadov, 2005).

Up to 1–1.5% of water resources are freshwater of which only 0.3% can be used. Freshwater resources are widely used in agriculture: water supply, irrigation, hydropower, inland navigation, fishing, etc. Significant pollution of rivers, lakes and seas with wastewater threatens to worsen the quality of water resources. 1 $m^3$ of wastewater pollutes 40–50 $m^3$ of natural river water. The main part of water resources in the Republic of Azerbaijan is river water. As we know the world's freshwater resources are being depleted. This is due to the uneven distribution of water resources and global warming. As a result, the world's population is increasingly suffering from water shortage (Gadirova, 2017).

A well-organized monitoring process facilitates the protection of the ecosystem. It is better to conduct preliminary studies on the objects and parameters to be identified before starting the monitoring (Gadirova, 2019). Azerbaijan is an oil country. Therefore the wastewater discharged from the refinery and other industries is mixed with sewage and eventually discharged into the Caspian Sea. As result seawater is contaminated with various pollutants (Gadirova, 2020).

The Caspian Sea is a very sensitive ecosystem. Over the past decades under the influence of anthropogenic and biochemical factors, the state of the ecosystem, in general, has deteriorated sharply especially in the northeastern part of the sea (Hense, 2003). Observations made in 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 (Kostianoy, 2005). Industrialization and urbanization in the Caspian region have developed rapidly over the past several decades and the associated increase in hydrocarbons is a concern in the region (Korshenko, 2005).

Offshore production and accidental oil spills, industrial wastewater, discharges flowing down from river water are considered the main sources of anthropogenic hydrocarbons in the marine environment. The industry is believed to be the main source of oil pollution in the Caspian Sea (Pat. 2011). 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 (Pat. 2011). 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 phenols was 0.002–0.003 μg/g (Hajiyeva,

2020). Pollution of water and bottom sediments are noted throughout the Absheron Peninsula and in Baku Bay. Note that the main volume of pollution (90% of the total) enters the Caspian Sea with river runoff (Hajiyeva 2019).

**Materials and methods:**

The quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) and 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. 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 (Hajiyeva 2020).

Phenol is an industrially important compound and ranks 33$^{rd}$ among the substances synthesized in the world. It is a very important compound from an industrial point of view. Thus phenol and its derivatives are definitely found in wastewater. Such water is discharged into water bodies and becomes a source of danger because chlorinated derivatives of phenol are very dangerous for aquatic ecosystems. In this connection, water samples were taken from 7 different areas of the Caspian Sea and then analyzed. Table 1 shows the names of these areas and the amounts of phenol found in the water samples. Phenol and its derivatives such as PAHs are considered hazardous to aquatic ecosystems (Hajiyeva S.R., 2020). Side effects occur at a phenol concentration of more than 1 g/l and at concentrations less than 0.5 g/l there is practically no harmful effect. At a phenol concentration of 0.2 mg/l such waters have an unpleasant taste. Chlorinated phenol derivatives are more dangerous(Phenol, 2021). They have a pungent odor. Even

with the chlorination of phenol derivatives at a concentration of 0.001 mg/l such waters have a negative effect. Too much phenol in water is damaging to living things. It causes serious illness in aquatic life and through the food chain poses a threat to human health (Yunker, 2002).

PAHs were also analyzed in water samples taken from those areas. It should be noted that some of these areas are beach areas and high levels of PAH in the water cause skin cancer. The results of the water analysis are shown in Table 2.

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. As you can see this indicator is mainly found in Hovsan and then in Guneshli. This is because there is an industrial plant in the area located near Hovsan and the water in Hovsan can be considered more polluted due to the constant discharge of wastewater (Hajiyeva S.R., 2018).

The standard values for the analyzed water samples are shown in Table 3. However, the analysis of the water samples shows that there are deviations from these standards. The difference in the amount of PAH, as well as phenol and its compounds, is evidenced and the pH (with PHS-25) values in water samples practically do not coincide with the standard values (Hygienic standards GN 2.1.5.1315-03, 2003).

Table 1

Phenol and its derivatives in water samples taken from the Caspian Sea

| Phenol, mg/l | Sahil | Shikov | Boulevard | Guneshli | 28 may | Hovsan | Bilgah |
|---|---|---|---|---|---|---|---|
| phenol | 0.14 | 0.10 | 0.14 | 0.12 | 0.13 | 0.16 | 0.08 |
| o-cresol | 0.06 | 0.02 | 0.03 | 0.02 | 0.04 | 0.45 | 0.01 |
| 2-nitrophenol | 0.16 | <0.04 | 0.04 | 0.04 | 0.10 | 0.12 | 0.02 |
| 2,4-dimethylphenol | 0.15 | 0.02 | 0.04 | 0.03 | 0.11 | 0.13 | 0.03 |
| 2,4-dichlorophenol | <0.02 | <0.02 | <0.02 | <0.02 | 0.03 | 0.04 | 0.04 |
| 2,6-dichlorphenol | 0.11 | 0.02 | 0.04 | 0.12 | 0.07 | 0.08 | 0.06 |
| 4-chloro-3-methylphenol | 0.21 | <0.04 | 0.05 | 0.05 | 0.14 | 0.06 | 0.04 |
| 2,4,5-TCP | 0.09 | <0.04 | <0.04 | 0.08 | 0.07 | 0.10 | 0.06 |
| 2,4,6-TCP | 0.10 | <0.04 | <0.04 | 0.09 | 0.07 | 0.10 | 0.06 |
| 2,3,4,6-tetrachlorophenol | 0.09 | <0.04 | <0.04 | 0.08 | 0.10 | 0.09 | 0.07 |
| pentachlorphenol | 0.14 | <0.04 | <0.04 | 0.12 | 0.12 | 0.16 | 0.04 |

Table 2

PAHs in water samples taken from the Caspian Sea

| Polysilic aromatic hydrocarbons, mg/l | Guneshli | Hov-san | Shikov | Boule-vard | 28 may | Sahil | Bilgah |
|---|---|---|---|---|---|---|---|
| Naphthalene | 0.09 | 0.19 | 0.07 | 0.04 | 0.07 | 0.02 | 0.01 |
| Achenthylene | <0.01 | <0.01 | <0.01 | <0.01 | 0.03 | 0.01 | 0.01 |
| Acenaften | 0.01 | 0.01 | <0.01 | 0.05 | 0.04 | 0.03 | 0.02 |
| Fluoren | 0.04 | 0.07 | 0.04 | 0.07 | 0.24 | 0.02 | 0.02 |
| Fenantren | 0.09 | 0.17 | 0.06 | 0.17 | 0.29 | 0.04 | 0.03 |
| Anthracene | 0.01 | 0.01 | <0.01 | 0.01 | 0.04 | 0.04 | 0.02 |
| Fluoranten | 0.01 | 0.01 | <0.01 | 0.01 | 0.03 | 0.01 | 0.01 |
| Piren | 0.01 | 0.01 | <0.01 | 0.01 | 0.05 | 0.01 | 0.00 |
| Benz (a) anthracene | <0.01 | 0.00 | <0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| Chrezen | 0.02 | 0.01 | <0.01 | 0.01 | 0.02 | 0.01 | 0.01 |
| Benz (b + j + k) fluorantene | 0.01 | 0.03 | 0.03 | 0.03 | <0.01 | 0.02 | 0.02 |
| Benz (a) pyrene | 0.01 | 0.01 | <0.01 | 0.01 | <0.01 | 0.01 | 0.01 |
| Inden (1,2,3-cd) pyrene | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 |
| Benz (ghi) perilen | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 | 0.01 |
| Dibenz (ah) antracen | <0.01 | <0.01 | <0.01 | <0.01 | 0.02 | 0.02 | 0.01 |
| Σ 15 Individual PAH | 0.35 | 0.56 | 0.31 | 0.46 | 0.88 | 0.28 | 0.19 |

Table 3

Standard chemical parameters of taken water samples

| Areas | pH | Phenols, mg/l | ΣPAH, mg/l |
|---|---|---|---|
| Guneshli(B3) | 6-7 | 0.04 | 0.01 |
| Shikov (S2) | 6-7 | 0.04 | 0.01 |
| Boulevard(S3) | 6-7 | 0.04 | 0.01 |
| 28 may(A3) | 6-7 | 0.04 | 0.01 |
| Bilgah(D3) | 6-7 | 0.04 | 0.01 |
| Sahil(S1) | 6-7 | 0.04 | 0.01 |
| Hovsan(C3) | 6-7 | 0.04 | 0.01 |

Table 4 shows the physical and chemical characteristics of the water samples. The water samples were collected and analyzed in March and off the coast. Analyses for all the water samples were performed in the same way.

Table 4

Physical-chemical parameters of the 7 water samples taken from the Caspian Sea

| Areas | Tem. °C | pH | Salinity, % | Electrical conductivity, mS/sm |
|---|---|---|---|---|
| Guneshli | 26.7 | 8.4 | 11.2 | 18.9 |
| Shikov | 26.2 | 8.1 | 11.2 | 18.6 |
| Boulevard | 26.4 | 8.2 | 11.0 | 18.8 |
| 28 may | 26.3 | 8.2 | 11.0 | 18.7 |
| Bilgah | 26.8 | 8.0 | 10.7 | 18.4 |
| Sahil | 25.8 | 7.8 | 10,3 | 17.5 |
| Hovsan | 26.1 | 8.7 | 10.8 | 18.2 |

As can be seen from Table 4 the water samples differed slightly in temperature which is due to the closeness of the average temperatures in these areas. This can be expressed by the presence of various salts in the water.

It should be noted that currently in our country serious work is underway to maximize the purification of wastewater discharged into the Caspian Sea using nanotechnological methods but the use of these methods in the industry requires a certain amount of time.

**Results and discussion:**

Water samples were taken and analyzed from 7 different regions of the Caspian Sea. The aim was to compare the levels of organic toxic substances – PAHs and phenolic compounds water samples taken from 7 different locations in the Caspian Sea.

It should be noted that all water samples were analyzed in the same manner. In general, the analysis of seawater shows that the amount of phenol was maximum in the regions of C3, S3 and S1. The greater contamination with phenol and naphthalene of the water samples taken from the C3 area is due to the presence of industry nearby. As in the analysis of PAHs, the most dangerous naphthalene was observed in the water sample taken from C3. Also in the water samples from A3 and C3 the maximum amount of 15 PAHs were detected.

Thus 15 PAHs, 9 heavy metals and 11 phenolic compounds were analyzed in water samples. In addition the pH, salinity and electrical conductivity of the analyzed water samples were determined. The pH values were found to be above the normal in the S1, S2, S3, A3, B3, C3, D3 water samples.

**Conclusions:**

1. Water samples were taken and analyzed in 7 different points of the Caspian Sea.

2. PAHs, phenol and its derivatives were determined in the water samples. Thus the content of PAHs, phenols and phenol derivatives in some analyzed water samples exceeded the permissible concentration.

3. More phenol was found in the water samples taken from the Sahil, Boulevard and Hovsan.

4. Naphthalene which is considered the most dangerous of the PAHs was found in the largest amount in the Hovsan area.

5. pH, salinity and electrical conductivity of the analyzed water samples were determined.

6. Chemical analysis was carried out by using very accurate analysis methods. In this regard, the GC-MSD gas chromatograph 6890N with a highly efficient mass-selective detecto-Agilent 5975 was used for the chemical analysis of organic toxic compounds.

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## РІВЕНЬ ОРГАНІЧНИХ ТОКСИЧНИХ СПОЛУК У ВОДНИХ ЕКОСИСТЕМАХ

**Проведено моніторинг проб води, відібраних із 7 різних регіонів Каспійського моря, та проаналізовано на наявність токсичних органічних сполук – ПАУ, фенолу та його похідних. Аналізи проводилися з використанням надзвичайно чутливих пристроїв, таких як газовий хроматограф GC-MSD 6890N з високоефективним масселективним детектором Agilent 5975. Було встановлено, що досліджувані токсичні органічні сполуки у стічних водах узбережжя Ка-**

**спійського моря перевищують гранично допустимі норми. Цей факт сформувався на тлі серйозних негативних впливів на флору та фауну Каспійського моря внаслідок скидання промислових стічних вод. У пробах води було проаналізовано 15 ПАВ та 11 фенольних сполук.**

***Ключові слова*: моніторинг; фенол; ПАВ; Каспійське море; водна система; аналізи.**

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## УРОВЕНЬ ОРГАНИЧЕСКИХ ТОКСИЧЕСКИХ СОЕДИНЕНИЙ В ВОДНЫХ ЭКОСИСТЕМАХ

**Проведен мониторинг проб воды, отобранных с 7 различных регионов Каспийского моря и проанализирован на токсичные органические соединения – ПАУ, фенол и его производные. Анализы проводились с использованием чрезвычайно чувствительных устройств, таких как газовый хроматограф GC-MSD 6890N с высокоэффективным масс-селективным детектором Agilent 5975. Было установлено, что исследуемые токсичные органические соединения в сточных водах побережья Каспийского моря превышают предельно допустимые нормы. Данный факт сформировался на фоне серьезных негативных воздействий на флору и фауну Каспийского моря в результате сброса промышленных сточных вод. В пробах воды было проанализировано 15 ПАУ и 11 фенольных соединений.**

***Ключевые слова*: мониторинг; фенол; ПАУ; Каспийское море; водная система; анализы.**

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