Chapter 01

Advanced Materials, Artificial Intelligence, and Sustainable Technologies for Energy and Environmental Engineering
ISBN: 978-9915-704-10-4
DOI: 10.62486/978-9915-704-10-4.ch01
Pages: 2-12

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Analysis of Toxic Substances in Seawater

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ABSTRACT

Environmental monitoring was conducted in two distinct regions of Caspian Sea. Hovsan is located on the coast of the southern Absheron Peninsula. Bilgah is located in the north of the Absheron Peninsula, on the coast of the Caspian Sea. Water samples were collected from the Hovsan and Bilgah areas and subsequently analyzed. Quantitative analyses were performed using the Agilent 6890N/5975 GC-MSD method. A total of 15 polycyclic aromatic hydrocarbons (PAHs) and 11 phenolic compounds were identified.The analysis revealed that the concentrations of organic toxic compounds in the water samples exceeded permissible limits. When comparing both areas, water samples taken from the Hovsan area were considered more polluted. Additionally, the physical-chemical parameters of the water samples from both Hovsan and Bilgah were determined.

Keywords: PAHs; Organic Compounds; Gas Chromatography; Environmental Monitoring; Seawater.

INTRODUCTION

It is very important to know the degree of pollution of seawater in the beach areas of the Caspian Sea. Since the Hovsan and Bilgah areas are beach areas, the increased level of water pollution in these areas is more dangerous. Pollution of sea water with polycyclic aromatic hydrocarbons is also a source of danger from the beach point of view; the increased risk of skin cancer is the most important of these factors.

The Caspian Sea is currently exposed to both pyrogenic and petrogenic pollution. On the other hand, against the backdrop of global warming, the decrease in the water level of the Caspian Sea is accompanied by an increase in the degree of water pollution and salinity. As a result, the aquatic ecosystem of the Caspian Sea is facing severe ecological pollution. Consequently, the Caspian National Park and beach areas are also affected by pollution. Seasonal ecological monitoring is conducted in these areas every year to assess the pollution levels of the seawater. Factors such as temperature, precipitation, and the discharge of other rivers and water flows into the sea significantly influence the degree of pollution. Considering the discharge of wastewater from the Oil Refinery located in the Baku area into the Caspian Sea, it is evident how severe the anthropogenic impacts are. As a result, the flora and fauna of the sea are seriously damaged. A clear example of this is the destruction and depletion of numerous fish species. Although the wastewater from the refinery is partially treated before being released into the sea, toxic

heavy metals and organic toxic substances still remain in the industrial effluent. Taking this into account, ecological monitoring has been carried out in the Caspian Sea. For the purpose of environmental ecological assessment, monitoring was conducted on water samples taken from two areas near the Caspian Sea; the chemical composition of seawater from the Bilgah and Hovsan regions was determined. Primarily, polycyclic aromatic hydrocarbons and phenolic compounds were analyzed in the oil-contaminated wastewater.

Organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), present a global environmental challenge due to their potential to cause inflammation and skin cancer. There are two primary anthropogenic sources of hydrocarbons: petrogenic and pyrogenic sources. Petrogenic sources encompass crude oil and petroleum-derived hydrocarbon compounds, while pyrogenic sources arise from the incomplete combustion of organic materials such as oil, wood, and coal.[1]

The Caspian Sea represents a highly sensitive ecosystem. Over recent decades, the condition of its ecosystems, particularly in the northeastern part of the sea, has significantly deteriorated due to both anthropogenic and biochemical factors. Observations in recent years indicate that the waters of the Caspian Sea, especially along the coast of the national park, are increasingly polluted by oil and sewage. The rapid industrialization and urbanization in the Caspian region over the past several decades, along with the associated rise in hydrocarbons, are major concerns for the area.

Offshore production, accidental oil spills, industrial waste, wastewater, and riverine discharges are considered the primary sources of anthropogenic hydrocarbons in the marine environment.[2,3] It is widely believed that industrial activities are the predominant source of oil pollution in the Caspian Sea. On average, approximately 2,342 million m^3 of industrial waste is discharged into the Caspian Sea annually, which contains around 122,5 thousand tons of oil, 1,1 thousand tons of phenols, and 9,9 thousand tons of organic chemical products. In the northwestern part of the South Caspian, the total hydrocarbon content is relatively low, ranging from 32 to 54,2 μg/g. In areas near oil fields, phenol concentrations are recorded at 0,002–0,003 μg/g.[4]

According to recent literature, it is reported that approximately 6 million tons of oil and oil products are discharged into the world's oceans every year.[5] Pyrogenic and petrogenic pollution, along with contamination from ballast water and other sources, contributes to the pollution of shared water bodies.[6] These segments of the hydrosphere function as dynamic systems, which over time leads to the reduction and depletion of freshwater supplies.[7,8] Pollution of water and sediment is evident throughout the Absheron Peninsula and in Baku, with the majority (approximately 90 %) of the pollution entering the Caspian Sea through river runoff.[9] The sources of seawater contamination by toxic organic compounds are well-known, but it is critical to implement stringent measures to prevent further pollution. This is particularly important as both PAHs and phenolic compounds pose significant risks to the flora and fauna of aquatic ecosystems.[10,11]

Experımental Part

The article examines the chemical analysis of seawater collected from two locations of the Caspian Sea for environmental protection purposes. Water samples were obtained from two sites using the "12 L Niskin" sampler at a depth of 0,5 meters below the sea surface, specifically from the Bilgah and Hovsan areas. Chromatographic analyses were conducted using a gas

chromatograph with a flame ionization detector (GC-FID 6890, Agilent, USA), equipped with a ZB-1 column (Phenomenex, USA). Helium was utilized as the carrier gas in the analysis. The identification of organic toxic substances in the seawater samples from the Bilgah and Hovsan areas was supported by the Caspian Ecology Laboratory. Ultimately, 15 polycyclic aromatic hydrocarbons (PAHs) and 11 phenolic compounds were analyzed in the water samples.

RESULTS AND DISCUSSION

The problem of water pollution in the world is currently one of the most pressing issues. Azerbaijan is also facing the same problem in this regard. Therefore, since it is an oil country, the problem of pollution of the Caspian Sea is always relevant. Pollution of sea water against the background of pyrogenic and petrogenic pollution is also very dangerous for the flora and fauna of that ecosystem. On the other hand, since beach zones have been created on many coasts of the Caspian Sea due to the development of tourism, it is very important that sea waters are clean. In this regard, since the Bilgah and Hovsan areas of the Caspian Sea are also beach areas, ecological monitoring was mainly carried out in these analyses.

The concentration of PAHs in the analyzed water samples is presented in Table 1 below. The chromatograms obtained are illustrated in figures 1 and 2. The maximum permissible concentration for polycyclic aromatic hydrocarbons (PAHs) is 0,01 μg/L. The results indicated that the measured PAH levels in many cases exceeded this regulatory limit.

Table 1. Amount of the PAHs in the water samples taken from Hovsan and Bilgah

PAHs, μgL^{-1} μgL^{-1} = $mkgL^{-1}$(or 0,001gL^{-1})	Hovsan	Bilgah
Naphthalene	0,19	0,01
Achenthylene	<0,01	<0,01
Acenaften	0,01	0,02
Fluoren	0,07	0,02
Fenantren	0,17	0,03
Anthracene	0,01	0,02
Fluoranten	0,01	0,01
Piren	0,01	0,00
Benz (a) anthracene	0,01	0,00
Chrizen	0,01	0,01
Benz (b + j + k) fluorantene	0,03	0,02
Benz (a) pyrene	0,01	0,01
Inden (1,2,3-cd) pyrene	0,01	0,01
Benz (ghi) perilen	0,01	0,01
Dibenz (ah) antracen	0,01	0,01

Based on the analysis, 15 PAHs were identified in the water samples, and it is important to note that the standard permissible concentration for PAHs is 0,01 μg/L. Table 1 illustrates that certain PAHs were present in concentrations significantly higher than the allowable limit. Among these, naphthalene was identified as the most hazardous. The amount of naphthalene in the water sample from Hovsan was higher than in the sample from Bilgah; however, in both cases,

the concentration exceeded the permissible limit.

The amount of naphthalene in the seawater sample extracted from Hovsan was approximately 19 times higher than in the sample taken from Bilgah.[12] Naphthalene is considered highly dangerous, as it can significantly impact erythrocytes in humans, potentially leading to their destruction. According to the International Agency for Research on Cancer (IARC), naphthalene is classified as a carcinogenic substance for both humans and animals. Scientists have placed naphthalene among the most toxic substances, often referring to it as a "chemical substance that causes death." This compound can enter the body through the respiratory system, where it exerts a carcinogenic effect. Fluorene, while a toxic organic substance, has not been found to possess the carcinogenic properties of naphthalene. Phenanthrene, a polycyclic aromatic hydrocarbon consisting of three fused benzene rings, is often found in cigarette smoke and has irritating properties that can cause the skin to become sensitive to light. Phenanthrene appears as a blue fluorescent white powder. Research conducted in the United States first identified phenanthrene as a substance associated with genetic mutations caused by exposure to smoking. This toxic compound is known to induce mutations that may lead to cancer.[13]

The results presented in the table indicate that the concentration of polycyclic aromatic hydrocarbons (PAHs) in the seawater samples from Hovsan was exceptionally high. Both pyrogenic and petrogenic pollutants play a significant role in this contamination.[14]

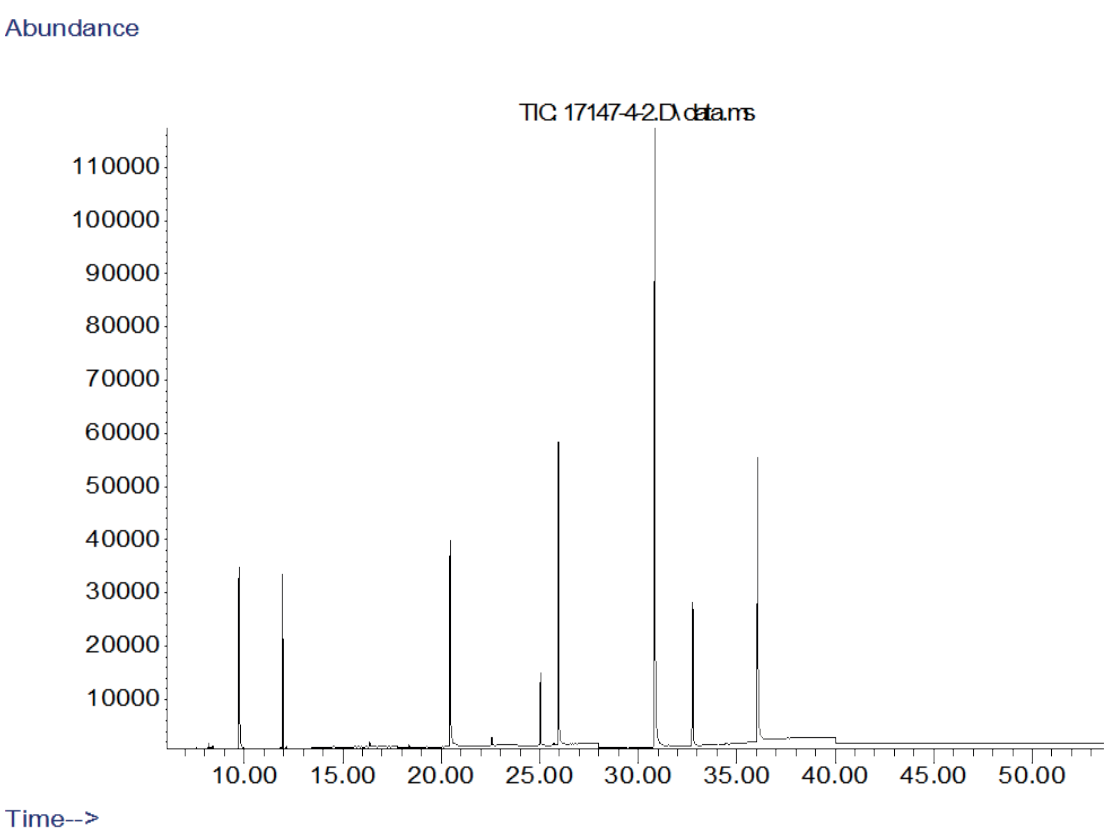


Figure 1. GC-MSD analysis of sea water sample taken from Hovsan (for PAHs)

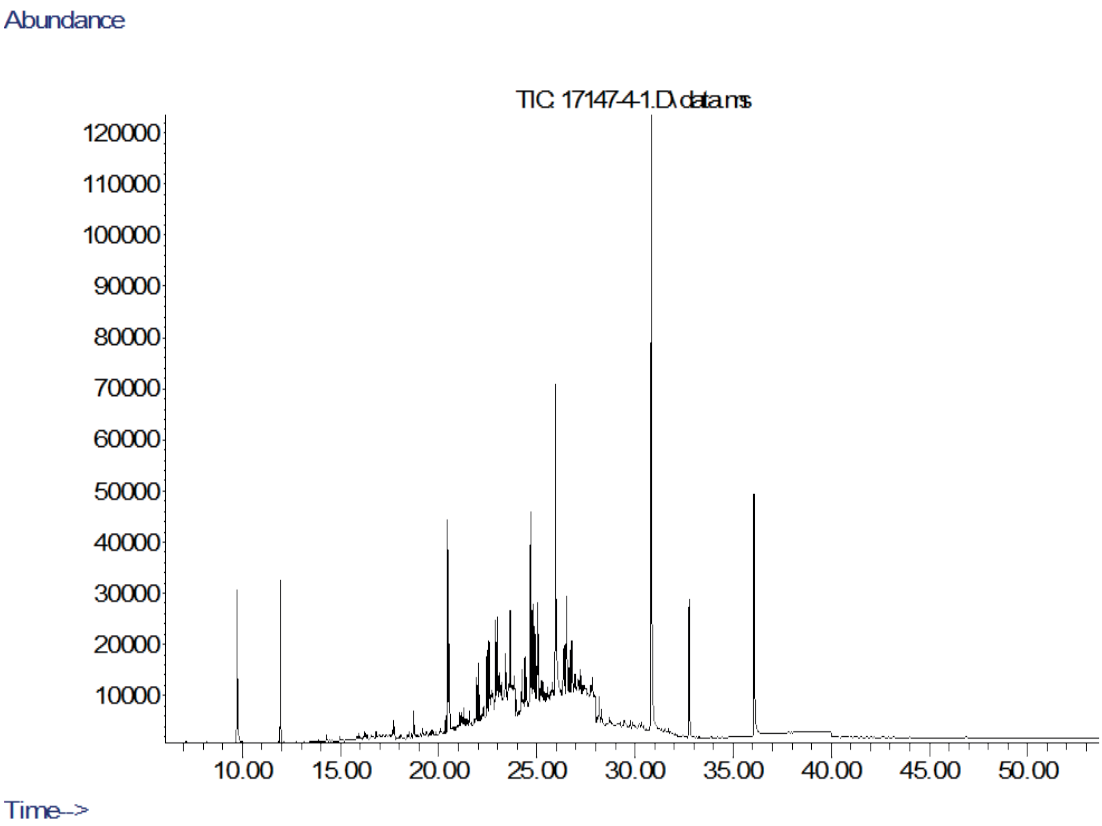


Figure 2. GC-MSD analysis of seawater sample taken from Bilgah (for PAHs)

Phenol and its derivatives, such as polycyclic aromatic hydrocarbons (PAHs), are considered hazardous to aquatic ecosystems. Lethal effects are observed when the concentration of phenol reaches 1 g/L, while concentrations below 0,5 g/L generally have no significant harmful effects. However, at a phenol concentration of 0,2 mg/L, the water begins to develop an unpleasant taste. The concentration of phenolic compounds in the analyzed water samples is presented in table 2.

The obtained chromatograms are shown in figures 3 and 4. Table 2 presents the results of the analysis of phenolic compounds in two seawater samples. It is important to note that phenolic compounds are considered hazardous to aquatic ecosystems when their concentration exceeds 0,01 mg/L in seawater (and 0,001 mg/L in drinking water). Chlorinated phenol derivatives are even more dangerous than phenol itself, as they have a pungent odor. Even at a concentration of 0,001 mg/L, chlorinated phenol derivatives in seawater can have a negative impact. Excessive levels of phenol in water are detrimental to living organisms, causing severe health issues in aquatic life. Furthermore, through the food chain, phenolic contamination can pose a significant threat to human health.[15]

As shown in table 2, the concentration of phenol in the water sample taken from Hovsan was higher than in the sample from Bilgah. The standard permissible concentration for phenol is 0,01 μg/L; however, the amounts detected in both the Hovsan and Bilgah water samples exceeded this limit.

Table 2. Amount of the phenolic compounds in the water samples taken from Hovsan and Bilgah

Phenol and its derivatives, μgL^{-1} μgL^{-1}= $mkgL^{-1}$(or 0,001gL^{-1})	**Hovsan**	**Bilgah**
phenol	0,16	0,08
o-kresol	0,04	0,01
2-nitrophenol	0,12	0,02
2,4-dimetilfenol	0,13	0,03
2,4-dichlorophenol	0,04	0,04
2,6-dichlorphenol	0,08	0,06
4-chloro-3-metilphenol	0,06	0,04
2,4,5-trichlorphenol	0,10	0,06
2,4,6-trichlorphenol	0,10	0,06
2,3,4,6-tetrachlorophenol	0,07	0,07
pentachlorphenol	0,16	0,04

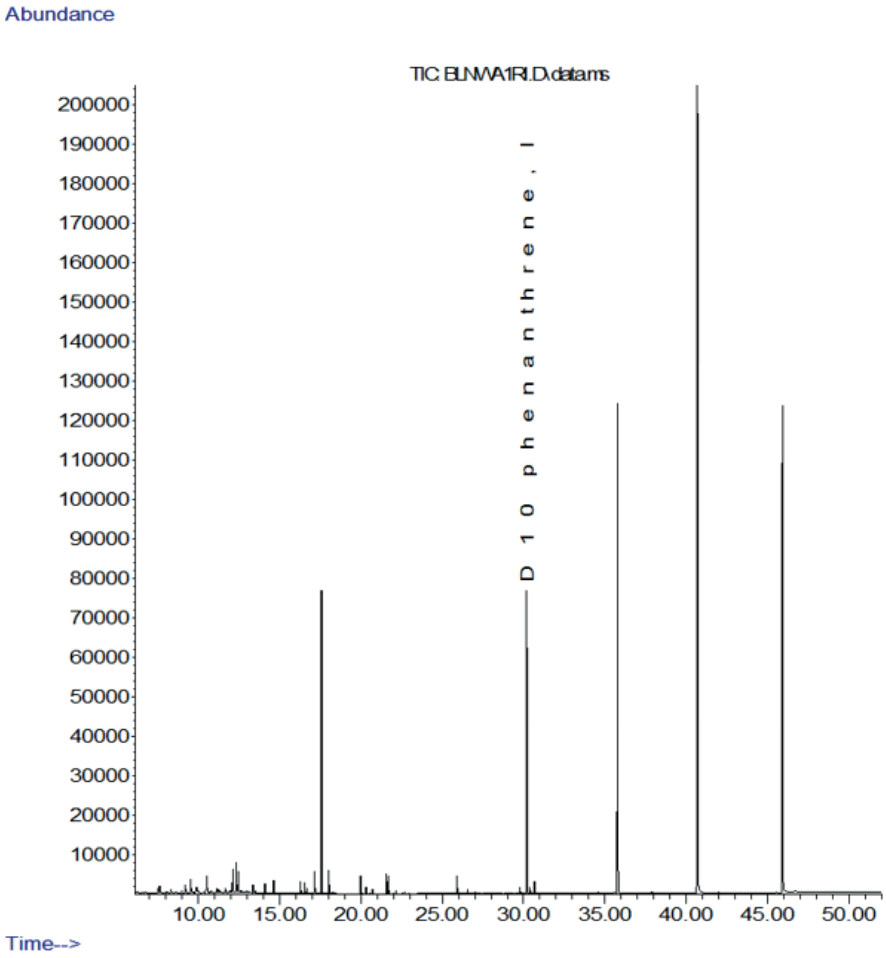


Figure 3. GC-MSD analysis of seawater sample taken from Hovsan (for phenolic compounds)

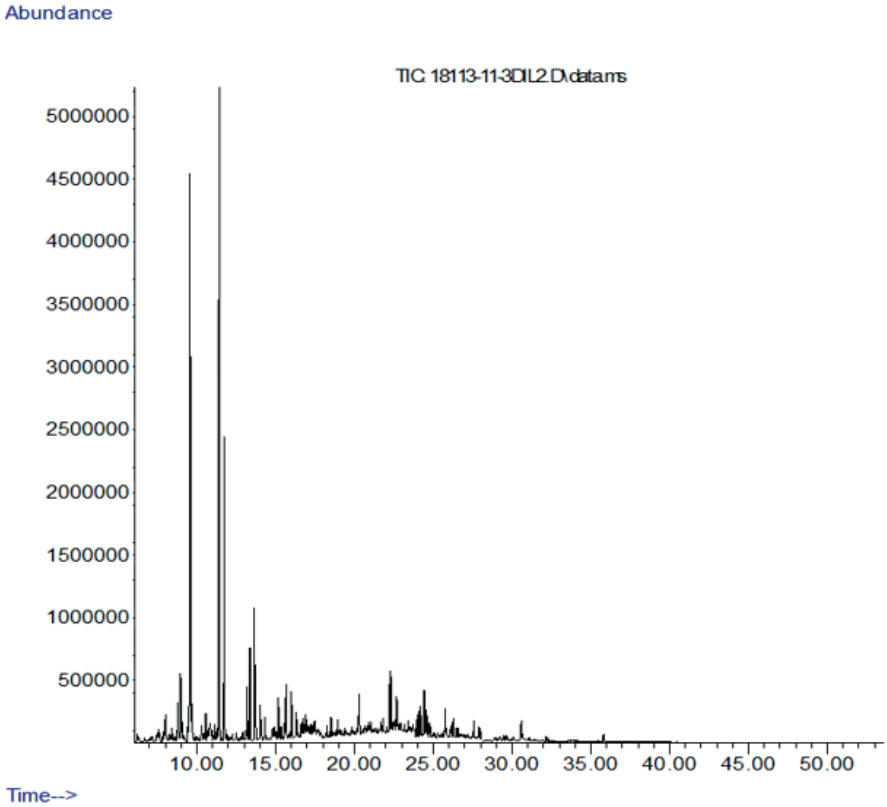
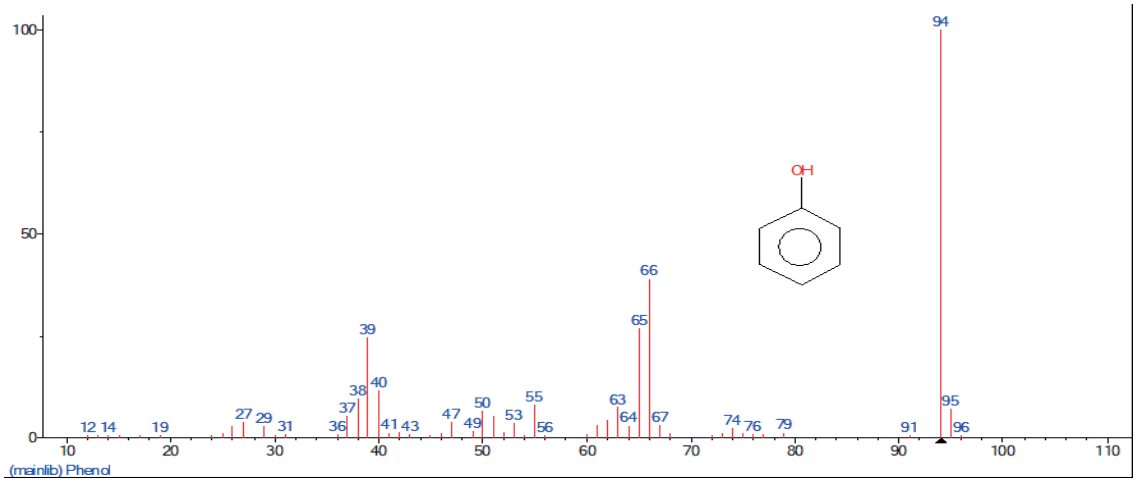
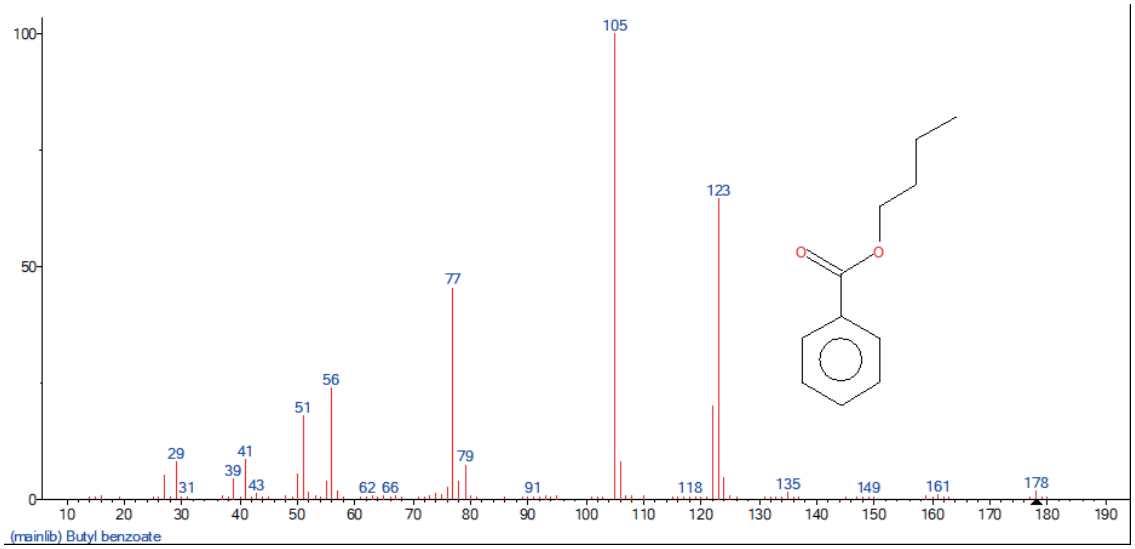


Figure 4. GC-MSD analysis of seawater sample taken from Bilgah (for phenolic compounds)

It should be noted that the content of toxic organic compounds in the water samples from both districts was above the permissible limits. Additional analyses were conducted on the water samples from Hovsan and Bilgah.



a. Phenol



b. Buthylbenzoat

Figure 5. Molecular spectra of some substances (a,b)

The molecular spectra (MS) of some of the substances obtained after the analysis process are shown below (figure 5 (a,b)). Molecular spectra provide information about the presence of substances in the analyzed sample based on their molecular mass.

Table 3 presents the physical and chemical characteristics of the analyzed water samples.

Table 3. Physical-chemical parameters of the water samples

Areas	tem. °C	pH	salinity, %	Electrical conductivity mS/sm
Hovsan	26,1	8,7	10,8	18,2
Bilgah	26,8	8,0	10,7	18,4

Although the physicochemical parameters of the seawater samples are within the normal range, the pollution caused by toxic organic substances has exceeded the permissible limits. The primary objective of the environmental monitoring was to assess the content of seawater by conducting chemical analyses.

CONCLUSIONS

1. Environmental monitoring was conducted in two areas of Azerbaijan.
2. Water samples were collected from the Hovsan and Bilgah areas and analyzed.
3. The analysis of the water samples included 15 PAHs, 11 phenols, and their derivatives.
4. The amount of naphthalene in the water sample from Hovsan was higher than in the sample from Bilgah, likely due to the presence of nearby industrial facilities.
5. The concentration of phenol in the water sample from Hovsan was greater than in the sample from Bilgah.
6. Quantitative analyzes were performed by the Agilent 6890N/5975 GC-MSD method.
7. The physicochemical parameters of the water samples from Hovsan and Bilgah were determined.

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FINANCING

None.

CONFLICT OF INTEREST

None.

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