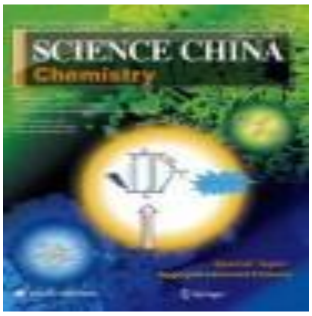

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Role of polyaromatic hydrocarbons in the pollution of aquatic ecosystems

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Polyaromatic hydrocarbons (PAH) are one of the most common pollutants entering surface water with effluent from oil refineries, shale refineries, wood chemical, coking, aniline dye industries, as a result of timber rafting, as well as from hydrolysis industry drains. During petroleum refining, catalytic and thermal cracking process produces polluted PAH waters, which are very dangerous for the environment. For the analysis of such waters, 3 samples were taken from the points of the Oil Refiner after preliminary and using analytical methods, we investigated the PAH and heavy metals in polluted waters. For samples 1 the PAH concentration was high, and for samples 2 and 3 the PAH concentration was relatively low. This is due to the fact that water samples taken from source 1 are closer to the site where the catalytic cracking process takes place; therefore, the PAH concentration is higher than in sites with samples 2 and 3. Qualitative analysis was performed on an HP6890 GC instrument with an HP5975 mass selective detector, GC-MS (Agilent, , USA) equipped with a ZB-5 column (Phenomenex, USA).

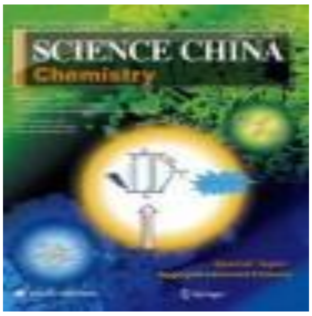
Keywords: *PAH, analytical methods, water, samples, pollutants , etc.*

Introduction:

Aromatic compounds enter the biosphere in various ways and their sources are industrial enterprises, transport, domestic wastewater. The particular attention given to aromatic compounds is largely due to their carcinogenic properties. Polycyclic aromatic hydrocarbons (PAHs) enter the atmosphere as a result of emissions and wastes from coke plants, some chemical plants, exhaust from internal combustion engines, and combustion products of various types of fuel. Groundwater is often contaminated with PAHs due to various sewage sludge.

Aromatic hydrocarbons in petroleum range from 5 to 55%. These are the most toxic components of oil, and at a concentration of only 1% in water, they kill aquatic lower plants. Oil, containing 38% of aromatic hydrocarbons, significantly inhibits the growth of higher plants, and with an increase in the aromaticity of oil, their herbicidal activity increases. The content of all groups of polycyclic aromatic hydrocarbons gradually decreases with the gradual transformation of oil in the soil.

Polycyclic aromatic hydrocarbons (PAHs) formed during fuel combustion are a multicomponent mixture, the individual analysis of each component of which is difficult without preliminary preparation of the sample for analysis. After preliminary chromatography of the sample by the method of column chromatography in a thin layer or by the method of differential sublimation, it is possible to analyze individual PAHs using UV spectroscopy. The method allows to determine the concentration of various PAHs in air up to 10-5%, or 0.1 µg / ml in solution.



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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 [1].About 6.1 million tons of oil products are thrown into the ocean annually, most of which are of anthropogenic origin. Before entering the open sea, these oil products pass through the entire coastal zone.

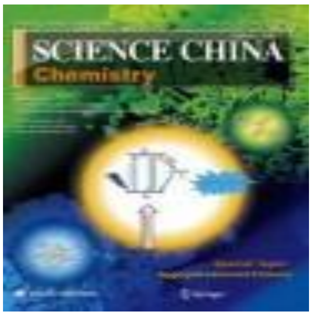
The Caspian Sea is a very sensitive ecosystem. Over the past decades, under the influence of anthropogenic and biochemical factors, the state of ecosystems in general has deteriorated sharply, and especially in the northeastern part of the sea [2].Observations of recent years show that the waters of the Caspian Sea, especially along the coast of the National Park, are also polluted by oil and sewage [3].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[4]. Industry is believed to be the main source of oil pollution in the Caspian Sea. The total amount of industrial waste discharged into the Caspian Sea averages 2342.0 million m3 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 phenols was 0.002-0.003 μg / g [4]. 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[5].

In the article reviewed, we analyzed wastewater taken from an oil refinery (refinery). It was important for us to calculate the amount of PAHs in these polluted waters. After purification, these 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[6].

Process:

As we know, PAHs are very dangerous for aquatic ecosystems. They have a deadly effect on the flora and fauna of the aquatic ecosystem.Water that is heavily contaminated with PAHs can cause skin cancer in humans.

For this reason we used a gas chromatography-mass spectroscopic method for the analytical determination of PAHs in wastewater taken from an oil refinery which is after cleaning discharged into the Caspian Sea. Dichloroethane for water extraction (GC-MS) was used to determine PAHs in aqueous samples. Then PAHs were determined in samples 1,2,3.



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Extraction was carried out in separating funnels previously cleaned with methylene chloride. Prior to the extraction, a mixture of compounds used as an internal standard was added to the seawater samples. Next, 50 ml of methylene chloride was added to a separatory funnel, and the contents of the funnel were vigorously shaken for several minutes. After peeling in a separating funnel, the organic part was separated from the aqueous. The procedure was repeated two more times. All three extracts were combined in a round-bottom flask and concentrated using a rotary evaporator at a water bath temperature of 30 ± 5 ° C to a volume of 2 ml, then dried under a thin stream of nitrogen and transferred to samplers in a volume of 1 ml. During the analysis of the samples, the solvents used were dichloromethane (Rathburn, Great Britain, Scotland) and n-pentane (HiPerSolv for HPLC, BDH, Great Britain, England) with chromatographic purity. For this, the solvents were preliminarily checked for purity using the gas chromatography method. Special precautions have been taken to prevent contamination from glassware, teflons, steel materials. Deionized water and methylene chloride were used to clean the dishes[7].

Qualitative analysis was performed on an HP6890 GC instrument with an HP5975 mass selective detector GC-MS (Agilent, USA) equipped with a ZB-5 column (Phenomenex, USA). The specifications of the ZB-5 column are as follows - 5% -biphenyl 95% -dimethylpolysiloxane copolymer, length - 60m, inner diameter 0.25mm, film thickness 0.25 μm. The volume of the injected sample is 1 μl[8].

A mixture of deuterated polycyclic aromatic hydrocarbons: naphthalene-d8, phenanthrene-d10, pyrene-d10, chrysene-d12, and perylene-d12 was used as an internal standard for calculating the obtained results of chromatographic analysis[9].

The discussion of the results:

Below are the chromatography-mass spectra of these wastewater samples: 1; 2; 3 and Table 1 show the results of analyzes for 16 PAH:

(naphthalene, acenaphthylene, acenaphthene, fluorene, phenenthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, indeno (1,2,3-cd) pyrene, benzo (ghi) perylene, dibenzo (ah) anthracene)

Mass spectrum of sample 1

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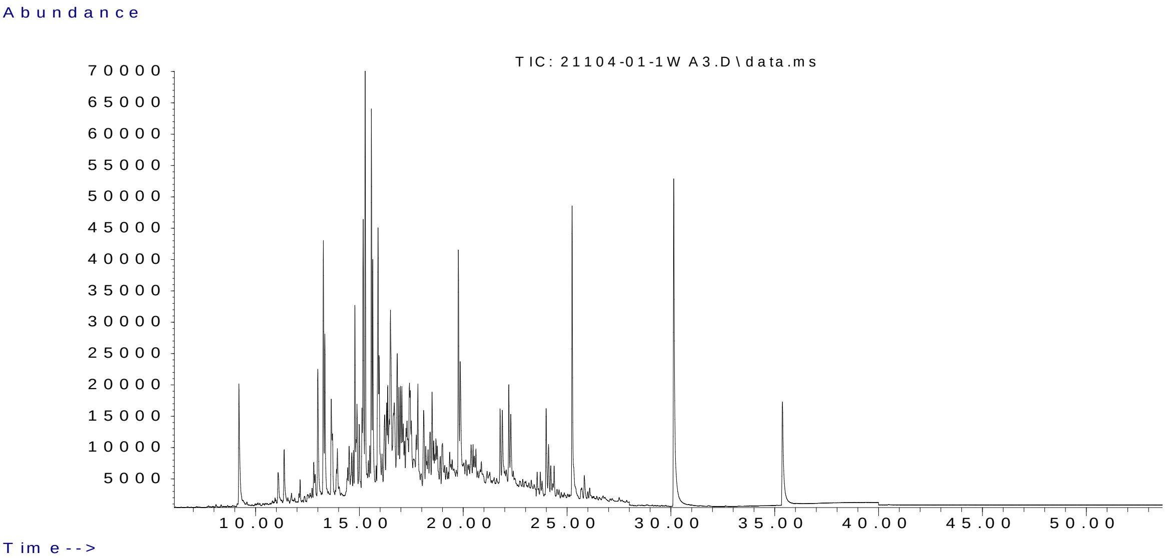
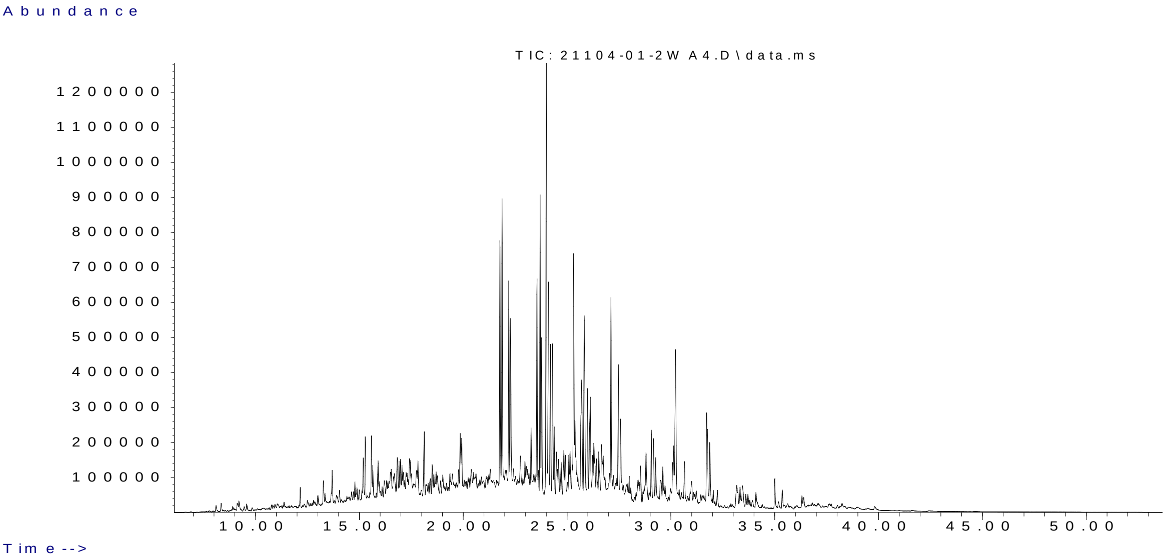
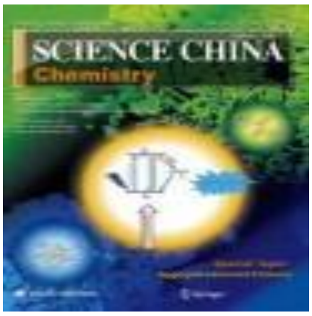


Mass spectrum of sample 2



Mass spectrum of sample 3



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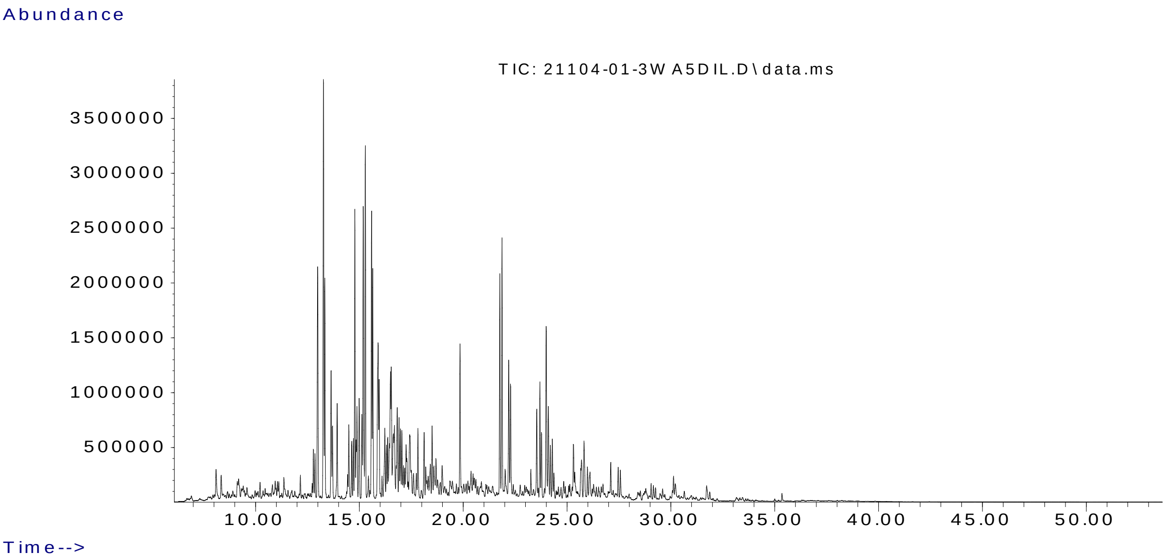

Table 1: Amount of PAH in Refinery Wastewater Samples

Analysis samples	1	2	3
	mkg/l (μq/l)		
Total EPA 16 PAH	**636**	**46**	**0,82**

It was found that the amount of PAHs in the analyzed samples is very high and exceeds the MPC for wastewater[10]. For different watercourses, the MPC for polyaromatic hydrocarbons ranges from 4246 to 709168 μg/l[11].

The table shows that the amount of naphthalene is very high and therefore such polluted waters are very dangerous for the flora and fauna of aquatic ecosystems[12].

Also these aqueous samples with emission method on a PerkinElmer ICP/OES-2100DV were determined by heavy metals and the results are entered in table 2.

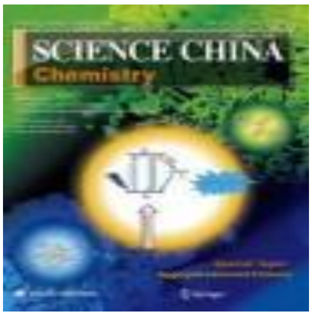

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Table 2: Amount of heavy metals in wastewater samples

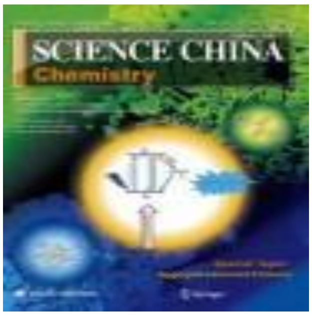
Heavy metals, mg/l	1	2	3
Fe	0,048	0,047	0,042
Zn	0,143	0,078	0,023
Cu	0,023	0,028	0,020
Mn	0,021	0,105	0,038
Pb	0,022	0,017	0,009
Cd	0,007	0,006	0,008
Cr	0,004	0,003	0,004
Co	0,009	0,014	0,012
Ag	0,009	0,010	0,008

All these metals are dangerous if they exceed the MPC norm, but Cd is more dangerous. MPC 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 MPC.

As you know, 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[13].The PAH concentration in the analyzed wastewater did not exceed the permissible value. This is a very good case, so wastewater treatment has proven to be effective (about 4246 μg/l for wastewater after cleaning) [14].

Conclusions:

1. Three water samples were taken from refinery and analyzed.
2. Chemical analysis of water samples was carried out on a GC-MSD gas chromatograph 6890N with a highly efficient mass-selective detecto-Agilent 5975.
3. In water samples on a PerkinElmer ICP/OES-2100DV heavy metals were analyzed.
4. In water samples the amount of PAHs did not exceed the permissible concentration.



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