

The Concentration of Trace Metals and Hydrocarbons Depending on Water Column Depth in Caspian Sea Taken from Areas of Azerbaijan

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Abstract: The present study was conducted to investigate the heavy metal contents (As, Ba, Cu, Ga, Mo, Rb, U, and V) and hydrocarbons (Total Hydrocarbons (THC) and 16EPA Polycyclic Aromatic Hydrocarbons (PAHs)) in seawater samples, which were collected at two different sites of Azerbaijan sector of the Caspian Sea. The Agilent 7700x Series ICP-MS (inductively coupled plasma mass spectrometry) with HMI (high matrix introduction) system applied to analysis seawater. Depending on concentration of elements from water columns depth can be explained in accordance with the geochemical system of classification of dissolved forms of elements in the sea water. Hydrocarbons are extracted with methylene chloride, after the extracts are cleaned on silica-gel columns and then injected into GC/FID (GC7890B, Agilent) for determination of THC and GC/MS (TRACE/DSQ, Thermo-Electron-Finnigan) operating in the selected-ion-monitoring (SIM) mode for determination of the 16EPA PAHs. The average concentrations of total hydrocarbons were below the admissible environmental levels. THC ranged from 20-29 $\mu\text{g/L}$ and PAHs from <10-29 ng/L , respectively.

Key words: ICP-MS, THC, 16EPA PAHs, GCFID, GC/MS SIM

1. Introduction

The Caspian Sea is the largest lake on our planet. It is bigger than the Great American lakes and Lake Victoria in Africa by surface area. However, it is unique not only because of its size. As distinct from other

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lakes, the water of the Caspian is not fresh, but brackish. Each liter of Caspian water contains 10-13 grams of salt making this water unsuitable for drinking or irrigation. However, the comparison of the Caspian water to oceanic water shows that it contains three times less salt than that of the World Ocean. Physically, the Caspian Sea is one of extremes. Its salinity varies greatly. Morphologically, the Sea is divided into three parts, the northern shallow part (average depth 6 m), and the middle section with an average depth of 190 m (maximum depth 788 m) and the southern Caspian with a maximum depth of 1025 m. The Caspian Sea occupies a deep depression on the boundary between Asia and Europe with a water level at present 27 m below sea level. It is approximately 1200 km long with a maximum breadth of 466 km, contains 79,000 km³ of water, and has a total coastline of more than 7000 km. The Caspian is fed by five major rivers or river groups: in the north the Volga (80% of total inflow) and the Ural (5%); in the west the Terek, Sulak and Samur (4-5%) and the Kura (7-8%); and, in the south, the short mountain rivers from the Iranian Alborz range (4-5%). Azerbaijan has more than 800 km of coastline along the Caspian Sea and almost the entire country is part of the Sea's catchment area. The littoral States of the Caspian Sea are the Republic of Azerbaijan, the Islamic Republic of Iran, the Republic of Kazakhstan, the Russian Federation and Turkmenistan [1-3]. Environmental problems of the Caspian Sea are multiple and various in their origin. On one hand, they are caused by the commercial use of the sea; on the other hand, human activity impacts coastal areas, including input from rivers in the Caspian. As the Caspian is an inland water body, anthropogenic (man-caused) impacts on catchment area (about 3.5 million km²) accumulate here. Anthropogenic impact on the Caspian ecosystem occurs concurrently with various natural endogenous and exogenous processes. It is primarily sea level changes, periodical seismic activity, surges and retreats, mud volcanoes and neo-tectonics. Special features of the Caspian include constant alterations of its area, volume, and configuration of the coastline and water column structure. Anthropogenic activity, as well as a natural impact, can have a chronic (long term) or acute (short term) effect. The sources of pollution are industrial, agricultural and accidental discharges and sewage. The main sources of pollution to the Caspian Sea have generally been considered to be offshore oil production and land-based sources, notably the Volga River. The presence of oil in the Caspian Sea region has been known since ancient times and the oil reserves were amongst the first to be exploited in the world. Baku was a centre for oil production at the turn of the 20th century and developed further development during the era of the Soviet Union. Exploration and exploitation, especially of offshore reserves, has blossomed since the breakup of the Soviet Union. Public opinion polls in the region have highlighted concerns about the oil and gas industry as a source of pollution to the environment of the Caspian Sea. Oil production areas cover vast areas of the coastal zone, particularly along the south coast of the Apsheron Peninsula in Azerbaijan. Population growth and industrial development in

the Caspian region have generated an immense pollution problem. Ten million people live adjacent to the Caspian Sea and 60 million more live in the Volga River watershed. The World Bank estimates that one million cubic meters of untreated industrial wastewater is discharged into the Caspian annually. Soviet oil extraction left behind polluted soil and water, rusty equipment, and well fires that burned for years. Meanwhile, the five countries surrounding the sea are rushing to exploit still untapped oil deposits.

Since the Caspian is an enclosed body of water, it has limited carrying capacity compared to larger and more open bodies of water. Pollution entering the Caspian is either bio geochemically altered, or remains in the Sea for years; none escapes and dilution is limited from external buffering waters. In the former Soviet Union, water and sediment quality measurements were taken on a regular basis and with good coverage. In Azerbaijan, the situation reported to be changing, and the number of monitoring surveys has increased. Within the current situation, over the same period the flux of pollutants into the Caspian has changed, with a drastic reduction in industrial and agricultural activity in Turkmenistan, Kazakhstan, the Russian Federation and Azerbaijan [4-5].

The present study was conducted to investigate the heavy metal contents (As, Ba, Cu, Ga, Mo, Rb, U and V), Total Hydrocarbons (THC) and 16EPA Polynuclear aromatic hydrocarbons (16EPA PAHs) of the Caspian seawater in Azerbaijan region, that were collected from 2 different sites with the geographic coordinates: ST#1- Easting 506,110 and Northing 4,456,694; ST#2- Easting 538,557 and Northing 4,431,454 at different depth of water column, in Azerbaijan region. It is known the analysis of ultra-trace elements in sea water samples is one of the most difficult analytical tasks in the field of environmental monitoring, as extremely low detection limits for elements buried in a highly saline matrix is required. The use of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for direct sea water analysis is currently limited by spectral and non-spectral interferences caused by the sea water matrix.

To avoid these problems the Agilent 7700x Series ICP-MS applied to analysis sea water. The Agilent 7700x ICP-MS combines the simplicity of a single collision cell mode (helium mode) for polyatomic interference removal with the superior matrix tolerance of its unique High Matrix Introduction (HMI) system. In order to reduce salt deposition in the nebulizer the humidifier is used. The humidifier humidifies the carrier gas and reduces salt deposition in the nebulizer. Third generation Octopole Reaction System (ORS3) cell technology provides higher sensitivity and more effective interference removal than ever before in complex, high matrix samples, eliminating the need for reactive cell gases in routine analysis. Helium mode on the ORS3 is so effective that interference correction equations can also be eliminated. These two factors redefine ease of use in ICP-MS, removing two of the most common causes of errors in multi-element analysis of complex samples.

Contact with oil in the environment as a result of the accident tanker accidents on oil platforms, drilling rigs, wells, as well as the release of any substance derived from crude oil, polluting the ecosystem of the sea water. Dealing with the consequences of such accidents take from several months to several years, depending on the degree of contamination. For example, recent incidents at sea have led to large amounts of crude oil being released and dispersed throughout the Gulf of Mexico.

One of the most frequently tested for groups of compounds within petroleum and petroleum distillates are Polynuclear aromatic hydrocarbons (PAHs). PAHs are comprised of aromatic rings which are strongly lipophilic. Larger PAH compounds are less water soluble and less volatile than smaller compounds and, therefore, pose more of a risk in nature. PAHs have been found to be carcinogenic, mutagenic, and teratogenic and can bioaccumulate within the environment. This being said, it is estimated that up to 30% (by weight) of crude oil are PAH compounds [6-9]. In environmental studies, the extent of PAH contamination as a group is often quantified by the concentrations of 16 of the representative PAH species, which are included in the list of priority pollutants as defined by USEPA [10-13]. Gas chromatography with mass spectrometry (GC/MS) is presently the preferred analytical technique for the analysis of PAHs. As is often the case in environmental analysis, effective sample preparation and cleanup holds the key of success for the analysis of trace PAHs.

2. Materials Methods

Water samples, collected from surface and bottom seawater layer with a 12-liter PVC Niskin sampler equipped with a Teflon-coated spring, suspended from stainless steel hydro wire and allowed to flush for 5 min before closing, in acid cleaned polythene containers for metals and in amber glass bottles for the hydrocarbons, packed and transported in ice-box for analysis. Surface samples were collected from all sites a depth not exceeding 5 meter (surface), whereas bottom samples were collected from sites a depths 50, 100, 200 and 350 meters.

For the metals, all plastic-ware sample bottles, pipette tips, filtration unit and flasks were soaked in 10% v/v HNO₃ for 24 h and rinsed with ultra-pure water before being used. Milli-Q ultra-pure water (resistivity 18.2 MΩ cm, pH (5.5–6.5) was used throughout, and all laboratory operations. In the laboratory by adding an appropriate volume of nitric acid the acid concentration of the samples are adjusted to approximate at 1% (v/v) nitric acid solution. An Agilent 7700x ICP-MS system was used to measure each sample in helium mode, using standard Agilent-recommended auto tuning for robust tuning conditions (around 1.0 % CeO/Ce). Agilent's new High Matrix Introduction (HMI) accessory for the 7700x and 7700s ICP-MS systems permits the direct analysis of samples containing percent level dissolved solids including neat seawater without prior dilution. The HMI accessory uses a combination of highly optimized robust plasma conditions and a

technique termed “aerosol dilution”. The net effect is a reduction in the amount of sample and solvent reaching the plasma and MS interface of up to 30x compared to a standard system. This reduction leads to higher plasma temperature, reduced suppression, improved stability and significantly lowers oxides.

The Agilent model 7700x ICP-MS using for analyze As, Ba, Cu, Ga, Mo, Rb,U and V in water samples. Multi-element calibration working standards solutions were prepared by appropriate dilution of from 10 mg/L multi-element stock standard solutions – (Part#8500-6940 in 5% HNO₃) in 1% HNO₃ correspondingly. The blank and calibration solutions were measured under optimized conditions. The calibration curve was automatically plotted by the instrument. Linear correlation coefficient (r) in all calibration curves were better than 0.9995. Instrument drift and matrix effects during measurement were corrected by using the internal standards include Sc, Ge, Rh, In, Tb and Bi were prepared by appropriate dilution from stock ICP-MS Internal Standard MixPart# 5188-6525 and added on-line at the time of analysis using a second channel of the peristaltic pump. For quality control purposes duplicate samples, matrix-spike sample were analyzed.

For the hydrocarbons, samples preserved at the time of sampling by the addition of a suitable acid to reduce the pH of the sample to less than 2.0. This accomplished by the addition of 5 mL of 1:1 HCl to a 1 liter of sample. Following collection and addition of acid, to sample must be cooled to $4 \pm 2^\circ$ C. Samples are extracted with methylene chloride by EPA Method-3510C (Separatory funnel Liquid-Liquid Extraction) and cleaned by EPA Method-3660B (Sulfur clean-up) and EPA-Method-3630C (Silica-Gel Cleanup) [14-19]. Concentrate extracts by Kuderna-Danish apparatus at 50-55°C till 2 ml and transfer extract into volumetric tube. After place the volumetric tube in nitrogen blow-down apparatus. Evaporate the extract till 1ml and the total hydrocarbons (THC) are analyzed on a gas chromatograph with a flame ionization detector (GC7890B, Agilent) and PAHs analyzed by GC/MS (Thermo-Electron, Finnigan) SIM modes.

GC/FID ANALYSIS

The hydrocarbons are analyzed on a gas chromatograph with a flame ionization detector (GC-FID) by GC7890B (Agilent), and the THCs are usually estimated by integrating the areas of peaks [20]. For GC/FID calibration mix used C7-C40 Saturated Alkanes (Sigma Aldrich, Cat#49452-U). Hexadecane-d₃₄ and squalane are using as internal standards for calculations and 5- α -Androstane as surrogate for the THC. The internal standard solutions are added to all samples and quality control samples just prior to extraction procedures. Chromatographic separation of THC was accomplished on a CP-Sil 5CB (100% dimethylpolysiloxane) capillary column (15 m \times 0.25 mm I.D., 0.25 mm film thickness). Nitrogen is the carrier gas and a pressure 15 psi (constant) is using for column elution. Sample injection was carried out in the split/splitless mode with an injection volume of 1 μ L. The GC oven temperature was programmed first

from 40°C (hold 2 min), 40°C to 320°C at a rate of 10°C/min (hold 2.0 min). FID temperature was 325°C (Make-up- 30 ml/min Hydrogen-30 ml/min, Air – 300 ml/min). The temperatures of the injection port were set at 300°C. Software acquisition is Chemstation, capable of continuous acquisition and storage of all data during analysis [22].

GC/MS-SIM ANALYSIS

A gas chromatograph/mass spectrometer (GC/MS) in selected ion mode (SIM) coupled to a capillary column is used to resolve, detect and quantitate polycyclic aromatic hydrocarbons (PAH) in solids at parts per billion levels. Samples are injected into a temperature-programmed GC/MS, operated in splitless mode. The capillary column is a DB-5MS (30 m x 0.25 mm ID and 0.25 mm film thickness). The mass spectrometer is capable of scanning from 50 to 500 AMU every second or less and uses 70 electron volts energy in electron impact ionization mode. Software – Thermo Electron-Finnigan Technologies Xcalibur 1.4SR1, capable of continuous acquisition and storage of all data during analysis. For identifications of components used 4 segments (in the each segments present 12 ions), for each segments scan time equal to 1.39s and dwell time 0.1 sec per ion [21].

The standard solutions is made from aliquots of mixture (Z-014J-PAK; M-525—SS-PAK; M-8310-SS-PAK, AccuStandard, Inc., USA) or pure compounds and diluted with dichloromethane to a final concentration of 0.25 ug/mL. The standards solution includes naphthalene-d8, acenaphthene-d10, phenanthrene-d10, pyrene –d10, chrysene-d12 and perylene-d12.

The internal standard solutions is added to all samples and quality control samples just prior to extraction procedures. Internal standards are used to calculate relative response factors and specific analyte concentrations based on retention time [22].

3. Results and Discussion

The results of analyses heavy metals and hydrocarbons in sea water samples taken in two sites at a different depth of surface (5 m), 50 m, 100 m, 200 m and 350 m. Depending on concentrations of analyses elements from depth of water column are demonstrated that for both sites there were nearly identical variation concentrations of As, Ba, Ga and V from depth of water column. Gradual decrease concentration with increasing water column depth was observed for elements Cu in station1 and in station2 respectively. Practically it is not significantly difference of the Mo, Rb and U concentrations in different column water depths in both site. In accordance with the geochemical system of classification of dissolved forms of elements in the sea water [23-24], the microelements in Tables 1 are subdivided into conservative (Mo, Rb and U),

biogenic (V, Ga, As and Ba) and lithogenic (Cu). Conservative-type trace metals interact only weakly with particles, and have concentrations that maintain a relatively constant (in space and time) ratio to salinity. Trace metals with conservative-type distributions in seawater such as Molybdenum, Rubidium and Uranium are involved in the major biogeochemical cycles of particle formation and destruction, but this is negligible relative to their concentration in seawater. Trace metals with biogenic-type distributions are significantly involved with the internal cycles of biologically derived particulate material. Their distributions are dominated by the internal cycle of assimilation by plankton in surface waters and the export production or transport of part of this material out of the surface layer followed by oxidation and remineralization of the bulk of this material in deeper waters. Consequently, their concentrations are lowest in surface waters where they are assimilated by phytoplankton and/or adsorbed by biogenic particles, and increase in the subsurface waters as sinking particles undergo decomposition or dissolution. Trace metals with lithogenic-type distributions have strong interactions with particles. Their concentrations tend to be maximal near major sources such as rivers, atmospheric dust, bottom sediments, and hydrothermal vents. Concentrations decrease with distance from the sources and, in general, the concentrations of the scavenged metals tend to decrease along the flow path of deep water due to continual particle scavenging [25-26].

Table 1. Concentration of metals in different depth of water column

Station	Depth	V	Cu	Ga	As	Rb	Mo	Ba	U
	metr	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
ST#1	Surface	0.788	0.852	0.996	1.475	8.166	16.873	12.095	6.324
	50	0.871	0.758	2.356	1.760	8.371	16.879	15.557	6.281
	100	0.944	0.723	2.789	2.726	8.852	16.939	26.686	6.278
	200	0.976	0.634	3.087	3.186	8.261	16.941	32.979	6.467
	350	1.026	0.626	3.603	3.414	8.759	17.075	44.166	6.362
ST#2	Surface	0.780	0.870	1.210	1.474	8.574	16.754	13.211	6.522
	50	0.807	0.799	1.708	1.659	8.695	16.771	16.382	6.657
	100	0.990	0.785	2.752	2.589	8.146	16.986	27.765	6.659
	200	1.031	0.672	3.468	3.211	8.285	17.185	34.639	6.618
	350	1.036	0.612	3.798	3.394	8.369	16.508	43.158	6.393

Table 2. Average concentration metals in sea water

	Depth	V	Cu	Ga	As	Rb	Mo	Ba	U
	metr	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average of both stations	Surface	0.784	0.861	1.103	1.475	8.370	16.813	12.653	6.423
	50	0.839	0.779	2.032	1.710	8.533	16.825	15.970	6.469
	100	0.967	0.754	2.770	2.658	8.499	16.962	27.225	6.469
	200	1.003	0.653	3.278	3.198	8.273	17.063	33.809	6.542
	350	1.031	0.619	3.701	3.404	8.564	16.792	43.662	6.377

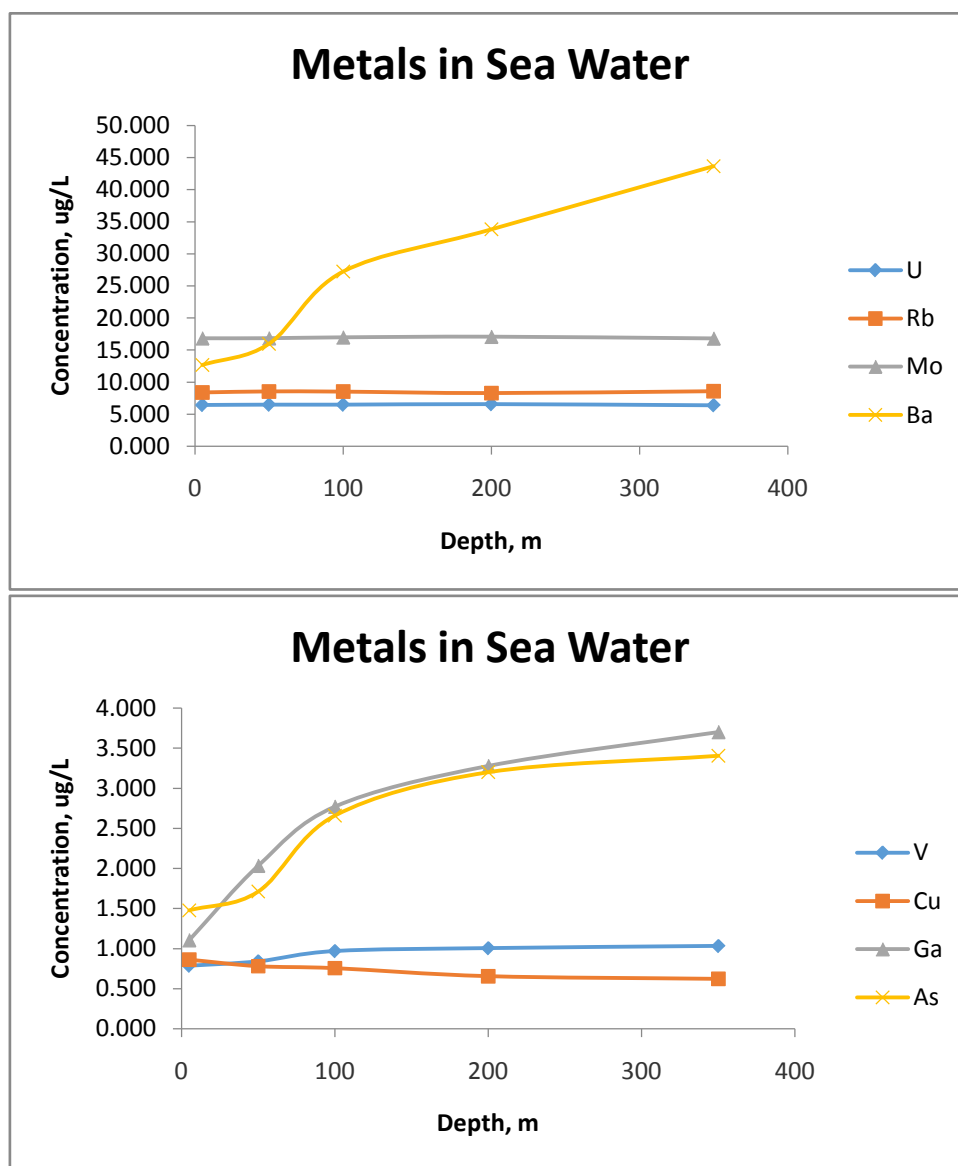


Figure 1. Dependence average concentrations of metal from water column depths.

4. Hydrocarbons

The residual of 16 polynuclear aromatic hydrocarbons (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, pyrene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene) and total petroleum hydrocarbons were investigated in Caspian sea water of Absheron areas.

Phenanthrene and fluorene were discovered on the surface and a depth of 50 m to 100 m. The concentration of the other components PAHs, these values were significantly lower the method detection limit (MDL=10 ng/L). And to a deeper depth (200 m and 350 m), all the components comply with values below the MDL (Table 3).

Table 3. Concentration of PAHs in different depth of sea water column.

Station	ST#1					ST#2				
	Surface	50	100	200	350	Surface	50	100	200	350
Naphthalene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Acenaphthylene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Acenaphthene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Fluorene	12	10	<10	<10	<10	13	11	<10	<10	<10
Phenanthrene	21	14	13	<10	<10	11	10	12	<10	<10
Anthracene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Fluoranthene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Pyrene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzo(a)anthracene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Chrysene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzo(b)fluoranthene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzo(k)fluoranthene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzo(a)pyrene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Indeno(123cd)pyrene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzo(ghi)perylene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Dibenzo(ah)anthracene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Total 16EPA PAHs	34	24	13	<10	<10	24	21	12	<10	<10

Because of the lower density of oil products, which remain on the water surface, on the surface, 50 m and 100 m hydrocarbons were relatively higher than at the depth sea water bottom. And the THC becomes about 20ug/L at deeper locations (Method detection limit for THC = 20 ug/L) (see tables 3-4 and figures 2-3).

Table 4. Average concentration THC and 16EPA PAHs in different depth of sea water column.

Depth, m	ST#1		ST#2		Average of both stations	
	THC	Total EPA 16	THC	Total EPA 16	THC	Total 16EPA PAHs
	ug/L	ng/L	ug/L	ng/L	ug/L	ng/L
Surface	29	34	25	24	27	29
50	28	24	23	21	26	23
100	27	13	21	12	24	13
200	22	<10	20	<10	21	<10
350	20	<10	20	<10	20	<10

These concentrations are much lower than that given by [27-29].

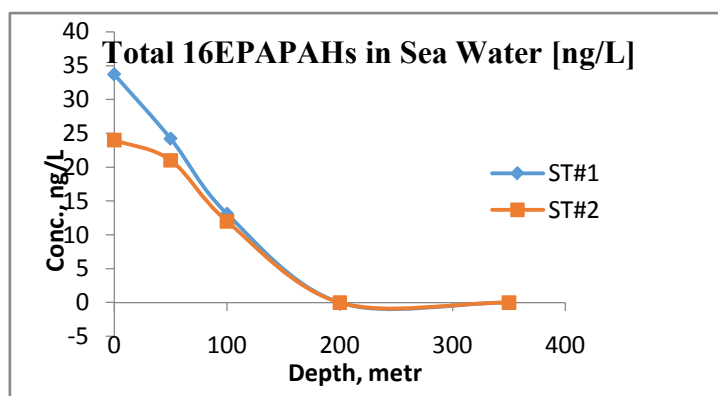


Fig 2. Concentration of Total 16EPA PAHs in different depth of sea water column.

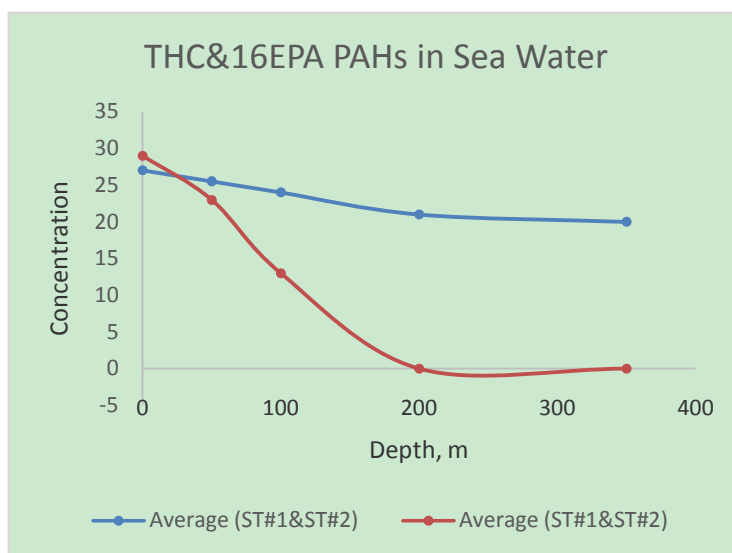


Figure 3. Average concentration THC and 16EPA PAHs in different depth of sea water column.

The THC concentration in seawater which can produce a harmful effect on the aquatic organisms is in the range of 50 µg/L in sea water. In our studies, the maximum value of THC concentrations equal to 29 µg/L, which is less than the value indicated by [27-29].

5. Conclusions

The Agilent 7700x Series ICP-MS (inductively coupled plasma mass spectrometry) with HMI (high matrix introduction) system applied to analysis seawater. Depend on concentration of elements from water column depths are different for investigated metals and can be explained in accordance with the geochemical system of classification of dissolved forms of elements in the sea water.

GC/FID (GC7890B, Agilent) and GC/MS (TRACE/DSQ, Thermo-Electron-Finnigan) operating in the selected-ion-monitoring (SIM) mode used for determination of the hydrocarbons and 16EPA PAHs, respectively. The average concentrations of total hydrocarbons were below the admissible environmental levels. THC ranged from 20-29 µg/L and PAHs from <10-29ng/L, respectively.

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390 **The Concentration of Trace Metals and Hydrocarbons Depending on Water Column Depth in Caspian Sea Taken from Areas of Azerbaijan**

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