Present Level of Petroleum Hydrocarbons in Seawater Associated with Offshore Exploration Activities from the Romanian Black Sea Sector *(Daniela Ţigănuș, Valentina Coatu, Luminița Lazăr, Andra Oros)*	**"Cercetări Marine" Issue no. 46** **Pages 98-108**	**2016**

PRESENT LEVEL OF PETROLEUM HYDROCARBONS IN SEAWATER ASSOCIATED WITH OFFSHORE EXPLORATION ACTIVITIES FROM THE ROMANIAN BLACK SEA SECTOR

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ABSTRACT

The objective of the study was to determinate the total content of petroleum hydrocarbons (TPH) in seawater of the Romanian Black Sea Sector during offshore exploration activities in February - June 2015. TPH concentrations in seawater samples, collected from 3 locations (depth from 200 to 1,625 m) were quantified by ultra-violet fluorescence spectroscopy. Petroleum hydrocarbons were present in all samples and their concentrations were highly variable, ranging from 28.8 to 271.3 (μg/L) with the mean of 110.2 ± 60.0 (μg/L), value significantly different to the average of 55.4 ± 86.3 (μg/L) recorded in the monitoring of seawater with offshore activities during 2011-2014. Over the 5-year period, the TPH concentrations in study area followed a steady increasing trend.
Key words: *total petroleum hydrocarbons, offshore exploration activities, Black Sea, seawater*

INTRODUCTION

Pollution is the main, most widespread and dangerous factor of anthropogenic impact on the hydrosphere. Pollution accompanies most kinds of human activities, including offshore oil and gas production and marine oil transportation. In the water environment, pollutants quickly spread over large distances from the sources of pollution. Stanislav Patin has pointed to in the book *"Environmental impact of the offshore oil and gas industry"* that the World Ocean has a large inertia of response to all forms of external impact. It requires a long hidden (latent) period to manifest the evidence of non-obvious consequences of this impact. The danger of the situation is complicated by the fact that when it happens, it will be too late to do anything [1].

Sources of petroleum hydrocarbons in the marine environment are both natural and anthropogenic and may come from natural oil seeps and oil spills. Oil

seeps from geological formations are the primary natural source. Inputs from natural sources are generally low compared to those from anthropogenic sources [2], [3]. In this study, the inputs from anthropogenic sources include discharges from oil and gas exploration and production activities and offshore oil and gas accidents[1]and 'near misses' [2] [4]. Offshore activities may generate huge amount of water which may contain chemicals and thereby may cause contamination in the sea water if are discharged into the ocean. There are various waste discharges associated with oil and gas activities; however, the major discharges to the marine environment are from drilling muds and cuttings and produced water[3] [5], [6].

Experience has shown that the accidents inevitably accompany offshore development. The most typical causes of accidents include equipment failure, personnel mistakes, and extreme natural impacts (seismic activity, ice fields, hurricanes, and so on). Their main hazard is connected with the spills and blowouts of oil, gas, and numerous other chemical substances and compounds. Following the explosion and oil spill from Deepwater Horizon on 20 April 2010, the European Union (EU) adopted the Offshore Safety Directive (2013/30/EU) to establish minimum requirements for preventing majors accidents in offshore oil and gas operations in the EU and to limit the consequences of such accidents.

Romania has a long history of oil and gas production, the exploration for hydrocarbon accumulations in the Romanian Black Sea continental shelf started at the beginning of the 1970s [7]. Offshore production of oil and conventional gas has been in decline since 1976 and 1986, respectively. Since 2009, when the dispute with Ukraine over the limitation of the continental shelf and exclusive economic zone in the Black Sea ended, Romania has extended its offshore exploratory activities [8]. The first deepwater wells Domino-1 in the Romanian sector of the Black Sea was drilled

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[1] Examples: Deepwater Horizon in the US in 2010 (11 killed), Montara in Australia 2009, Usumacinta in Mexico in 2007 (22 killed)

[2] Such as oil & gas leaks, failures of production process safety and drilling well control; failure due to invalid design change; high number of maintenance backlogs of safety critical elements. Recent incidents examples: Gullfaks C in May 2010, Gannet F, 2011; both in the North Sea

[3] OSPAR has, however, adopted Recommendation 2001/1 for the Management of Produced Water from Offshore installations. Under the recommendation each contracting party should ensure that the total quantity of oil in produced water discharged into the sea in the year 2006 has been reduced by a minimum of 15% compared to the equivalent discharge in the year 2000. The means used by the most of the contracting parties for achieving the goal of 15% reduction had been the re-injection of produced water.

See _Extract from the Annual Report of the OSPAR Commission 2006/07', OSPAR Oil and Gas Strategy, at: http://www.ospar.org/eng/doc/Annual%20Report%202006_7%20OIC.pdf (viewed: 15.08.08).

in early 2012. According to the preliminary estimates, the amount of reserves could well reach 84 bilion cubic metres of gas. OMV and Exxon Mobil announced figure of possible recoverable reserves of 40 bilion cubic metres.

The purpose of our study was to assess the extent of contamination by petroleum hydrocarbons within the vicinity of the Wellsite areas before and after drilling process was completed. In addition to this objective, the results of the monitoring offshore areas, both Pre-Drill and Post-Drill petroleum hydrocarbon concentrations during 2011-2015 were compared to regional baseline data and internationally and locally accepted environmental standards to determine the ecological significance of any deviations from background. The results from this study should provide the background information regarding the present level of petroleum hydrocarbon in seawater associated with offshore exploratory activities from the Romanian Black Sea Sector, which will be helpful for future studies on TPH pollution.

MATERIAL AND METHODS

The studied area is located on the Romanian Black Sea continental shelf between 30° 57 E to 31° 13 E and 43° 53 N to 44° 16 N, which is approximately 258 km off Constanta and 274 km and 220 km off Bulgaria and Ukraine, respectively, at depths between 200 and 1625 m. A total of 154 water samples were collected at 28 sampling stations from 3 locations within the offshore exploratory area during February - June 2015 (Fig. 1).

TPH concentrations in seawater samples were quantified by ultra-violet fluorescence spectroscopy. Extraction was carried out in hexane/dichloromethane: 7/3 (v/v). The organic layer was separated and dried over anhydrous sodium sulfate. Fluorescent method was use to determine the TPH concentration with Fluorat-02-3M analyzer at wavelength of 360 nm. The method detection limit for TPH was 5.0 (μg/L) [9].

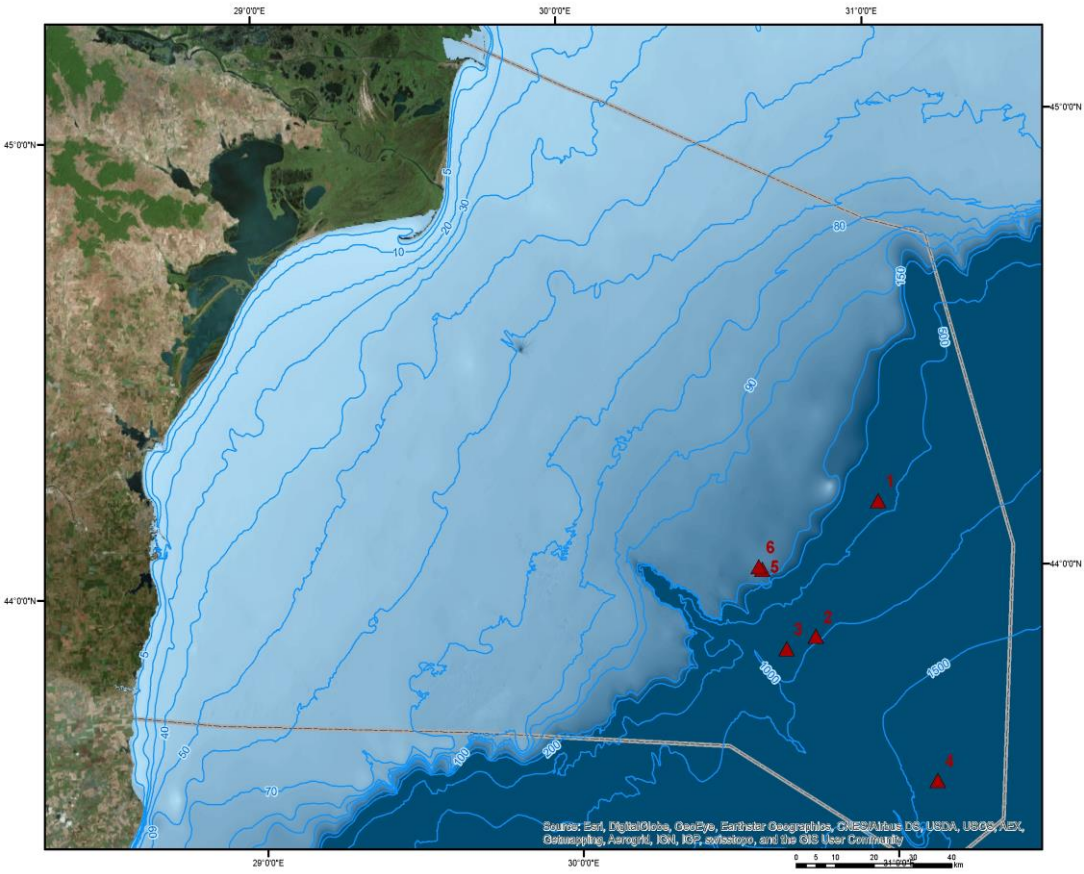

Fig. 1. Seawater sampling locations in Romanian offshore area
Source: Alina Spinu, N I M R D "Grigore Antipa", Constanta

RESULTS AND DISCUSSIONS

The total content of petroleum hydrocarbons was identified and determined quantitatively in 154 seawater samples collected during February - June 2015. Summary of statistical values of TPH concentrations before, during and after drilling processes in 2015 is given in Table 1.

Table 1. Descriptive statistical results of TPHs (µg/L) in seawaters of the Romanian Black Sea sector during offshore exploratory activities, February - June 2015

TPH exploratory activities	n	Mean	Median	Min.	Max.	percentile		Std. dev.
						the 25th	the 75th	
TPH before drilling	60	100.8	81.5	29.5	271.3	56.7	131.5	58.6
TPH during drilling	34	137.4	125.2	47.9	258.3	77.1	196.3	64.4
TPH after drilling	60	104.2	87.5	28.8	240.0	61.7	142.7	55.1
	154*	***110.2***	***87.1***	***28.8***	***271.3***	***66.3***	***165.4***	***60.0***

** number of seawates samples collected during offshore exploration activities, 2015*

The pollution level in seawater associated with offshore exploratory activities

In 2015, the different level of pollution with petroleum hydrocarbons in offshore seawaters during the drilling process compared with both the Pre-Drill and Post-Drill petroleum hydrocarbon concentrations is shown in box plots of TPH concentrations (Fig. 2).

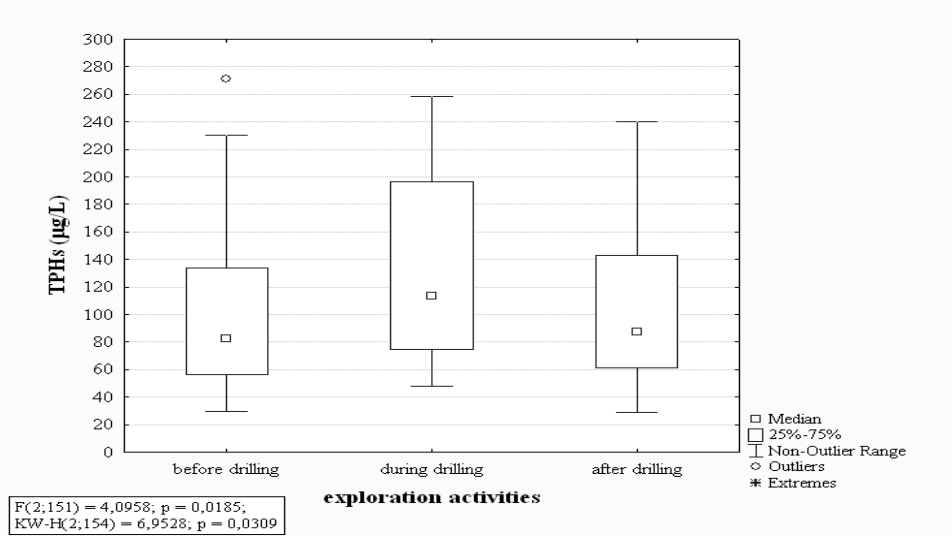

Fig. 2. Box plot of total TPH concentrations (µg/L) from seawater of the Romanian Black Sea sector during offshore exploration activities, February - June 2015

A significant difference ($p < 0.05$) was recorded between the concentrations that were determined during drilling activity, with a higher level of pollution (137.4 ± 64.4 μg/L) and those before (pre-) and after (post-) drilling process. Drilling operations are always associated with discharges of drilling fluids, muds and drill cuttings, activities that exert a pressure on the marine environment of short duration. The total content of TPH in seawaters after completion the drilling process (104 ± 55.1 μg/L) in 2015 showed a level of pollution similar to that before drilling process. These results indicate that the effects of discharges are local and of short duration and the risk of widespread impact from the operational discharges is low. One cannot ignore the possibility of cumulative effects from the operational discharges of drilling processes.

Compared with the results from the literature (Table 2) seawaters from offshore area, in 2015 after drilling processes, could be considered generally as moderately contaminated by TPHs (Table 1). Oppenheimer [10] has suggested that if the concentration of petroleum hydrocarbons in the seawater has exceeded the value of 100 (μg/L) should be considered to be polluted.

Table 2. Summary of literature data about total TPH concentrations in seawater from various marine sites in the world

Location	TPHs (μg/L)		References
	means	range	
offshore activities in the Artic			*[11]*
Russian shelf			
Pechora and Kara Seas		< 33	[12]
Mendeleev Rise region of the Artic		< 10*	[12]
Pechora Sea	15-19	2.0-87	[13]
White Sea	35-45	28	[14]
Kara Sea	60	8-406	[15]
other offshore areas in the world			*Post Drill Reports*
East coast of Trinidad	80-120		[16]
Levantine Basin, Israeli coastline	52±24	19 - 88	[17]
Romanian Black Sea Sector	78±81	6 – 758	Present study, 2015
offshore oil and gas accidents			
offshore blowout			
Ixtoc I Blowout, Gulf of Mexico		5-10600	[18]
Ekofisk Blowout, North Sea		< 300	[19]
Deepwater Horizon, Gulf of Mexico		60-260**	[20], [21], [22]
Coastal waters			
Bohai Bays, China	61-173	20–508	[23]
Romanian Black Sea Sector	134±159		national monitoring, 2011- 2015

**low concentrations <10 (μg/L) were found in water from Mendeleev Rise region, which is considered one of the least contaminated regions of the Artic and therefore suitable for measurements of background concentrations; ** mg/L*

In comparison with the results from some other studies, the mean of Post-Drill petroleum hydrocarbon concentrations in seawaters from the Romanian Black Sea Sector was higher than that from the Arctic regions (< 50.0 μg/L) [11], but comparable to that reported from exploratory wellsites of the East coast of Trinidad (< 120 μg/L) [16] and lower than that found in romanian coastal seawaters (< 134 μg/L, national monitoring programme of seawaters, 2011-2015) and in Bohai Bay, China Sea during 1996 – 2005 (<173 μg/L) [23]. In relation to environmental quality standard for seawater recommended by national legislation [24], 90% of measured concentrations of TPH in 2015 were within the allowed limit (<200 μg/L).

Statistical tests have showed that the TPHs were significantly different ($p < 0.05$) between the year 2015 with a mean of 110.2 ± 60.0 (μg/L) and the period 2011-2014 with a lower average of 55.4 ± 86.3 (μg/L) in seawaters that could be considered as slightly polluted compared with the results from the literature and environmental quality standard for seawater. Occasionally extreme values within the range of 246.0 – 758.0 (μg/L) were determined in 2 % of seawater samples during drilling processes in 2012 and 2014, probably due to the accidental oil spills and oil products (Table 2).

Table 2. Descriptive statistical results of TPHs (μg/L) in the seawater of the Romanian Black Sea sector during offshore exploration activities, during 2011 - 2014

Year	n	Mean	Median	Min.	Max.	percentile		Std. dev.
						the 25th	the 75th	
2011	20	19,6	19.7	11.0	26.8	15.7	*22.9*	4.4
2012	80	38.7	20.1	5.9	758.3	13.9	*29.3*	90.5
2014	116	73.1	45.0	19.9	650.0	35.9	*79.8*	87.0
2011-2014	***216***	***55.4***	***34.2***	***5.9***	***758.3***	***20.4***	***49.2***	***86.3***

In relation to environmental quality standard for seawater (Maximum Allowed Concentration - MAC) of 50.0 (μg/L) the measured concentrations of TPH in our study during 2011-2014 were within the allowed limit. Generally, the total petroleum hydrocarbon concentration in seawater which can induce harmful effect on the aquatic organisms is in the range of 50 (μg/L). Gordon and Prouse [25] reported that oil concentrations in excess of this value can retard phytoplankton photosynthesis. Most countries (eg. China and Russian Federation) use this concentration of 50 (μg/L) as seawater quality standard (China's Marine Monitoring Standards of GB 3097–1997 and Annex IV Sea Water Quality Standards in Russia). In comparison with the results from some other studies, the mean of TPH (55 ± 86 μg/L) in Romanian offshore area was comparable to that reported in Levantine Sea, around the drilling wellsites off the Israeli coastline (52 ± 24 μg/L) and was significantly higher than that from Mendeleev Rise region, which is considered one of the least contaminated regions of the Artic and therefore suitable for measurements of background concentrations (<10.0 μg/L) [12].

During 2011 - 2015, the TPH concentrations in seawaters from Romanian Black Sea continental shelf have followed a steady increasing trend (Fig. 3).

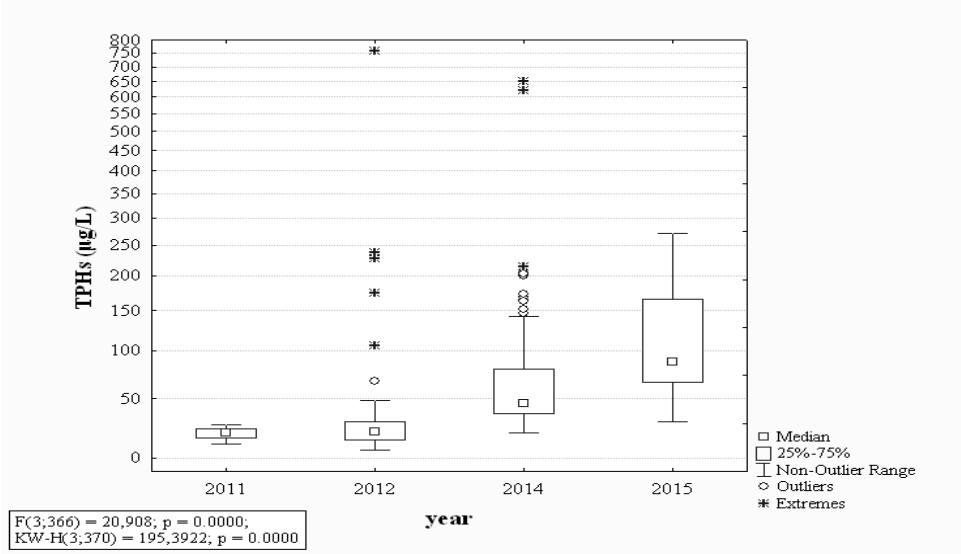

Fig. 3. Box plot for total petroleum hydrocarbon concentrations (µg/L) in seawater of the Romanian Black Sea sector during offshore exploration activities, 2011- 2015

The pollution level in seawaters associated with offshore oil and gas accidents

Offshore drilling operations are tremendously risky by producing accidents that include large oil spills and catastrophic oil blowouts. Significant TPH concentrations of 10.6 mg/L and 0.3mg/l were measured in seawater in the vicinity of the blowout of the exploratory well Ixtoc I located in the Bay of Campeche - Gulf of Mexico in 1979 and the exploratory well Ekofisk in the North Sea, in 1977 [18], [19]. The 2010 BP/Deepwater Horizon oil spill was one of the largest marine spills in the world [20], [21], [22]. In April 2010, the extreme high levels of TPHs were recorded in seawater of The Gulf of Mexico, that have varied from 60 to 260 mg/L. During 2011-2015 on Romanian Black Sea continental shelf there has been no accident during offshore exploration operations.

CONCLUSIONS

Seawaters from the offshore area in 2015 could be considered as moderately polluted by petroleum hydrocarbons. The results of our study indicate that during drilling processes the effects of discharges are local and of short duration and the risk of widespread impact from the operational discharges is low but one cannot ignore the possibility of cumulative effects from the operational discharges of drilling processes.

During 2011 - 2015, the petroleum hydrocarbon concentrations in seawater associated with offshore exploratory activities from Romanian Black Sea sector have followed a steady increasing trend. In relation to environmental quality standard for seawater recommended by national legislation the measured concentrations were within the allowed limit. Since 2011 and so far on Romanian Black Sea continental shelf there has been no accident during offshore exploratory operations.

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