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Analysis of Technogenic Load of Oil and Gas Production on Caspian Region

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Abstract. The problem of intensive pollution of the Caspian Sea has been continued to be one of the most significant and serious for the region. The rising of pollution level of the Caspian Sea coast with oil hydrocarbons has a particular concern. The purpose of this paper is to assess the pollution degree of the Caspian coast with petroleum hydrocarbons. The idea of the author is to provide a comprehensive analysis of the environmental destructive factors of the oil production process on natural complexes, including the effect of chemical pollution of the water basin with petroleum hydrocarbons on local hydrobionts. Methods of mathematical modeling of the oil films spreading on the water surface aimed to the prediction of the influence area, and methods of toxicological studies and assessment of the dose-effect relationship have been used. It was determined that the waters of the Caspian Sea, associated with offshore oil production, are areas of increased environmental risk. In the cases the concentration of hydrocarbons is above 1 mg / l, physiological changes are observed in the majority of dominant groups of hydrobionts. Areas of increased risk level for marine ecosystems caused by gas and oil industry development are connected with north and west-south parts of the Caspian Sea. The obtained results can be used to develop programs to ensure the environmental safety of the studied region.

Keywords: oil pollution, offshore oil production, marine biota, ecological risk, spills, Caspian Region, oil film, risk assessment, biodegradation, mathematical modelling.

1 Introduction

The discovery and development of a new oil and gas subprovince on the continental shelf of the Caspian Sea brought the region to the rank of one of the most promising areas for oil production in the 21st century [1]. The Caspian Sea is the largest in the world, unparalleled inland water area of more than 398 thousand square kilometers, not connected with the World Ocean. Currently, the proven oil reserves of the Caspian region are estimated at 5.4 billion tons (3.2 % of the world total), gas reserves are at the level of 8 trillion cubic meters (5 % of the world total) [2] (Figure 1).

Intensive oil production in the Caspian [3] entails a number of environmental problems. The technogenic load on the natural environment of the region is expressed both in the direct influence on the biota of chemical and physical factors, and indirectly by changing the habitat of marine hydrobionts.

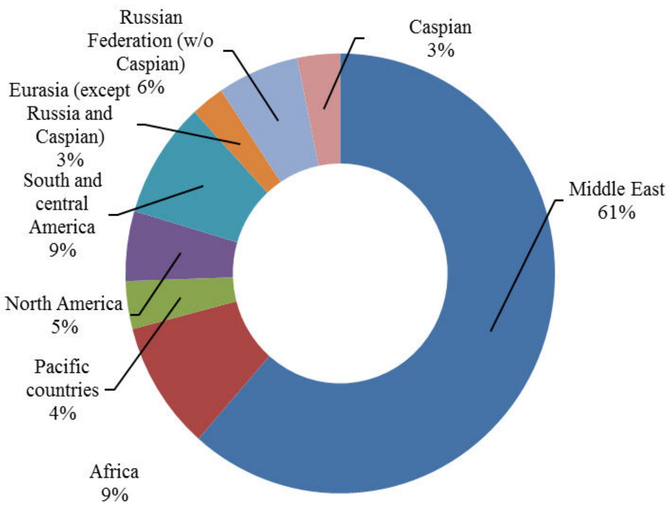

Figure 1 – Distribution of proven oil reserves

According to the Caspian Regional Thematic Center for Pollution Control (Caspian Environmental Program), up to 122.35 thousand tons of oil products enter the sea annually from various sources [4].

The situation is complicated by the ongoing processes of accumulation, decomposition and burial of incoming toxicants, which is typical of drainage reservoirs. Once released into the environment, oil may undergo a variety of natural processes that may act to reduce the severity of a spill, or accelerate the decomposition of the spilled oil into forms that are less environmentally hazardous. Five natural processes have been identified as particularly important to the fate of oil in the environment: weathering, evaporation, oxidation, biodegradation, and emulsification [5]. By their biological nature, products of oil transformation in the aquatic environment and their further combined interaction with other toxicants represent a high environmental hazard [6]. The development of toxic effects in aquatic organisms is determined mainly by the bioavailability of xenobiotics, the physicochemical parameters of the environment, and mainly the individual characteristics of the organism. The degree of susceptibility depends on the level of organization and physiological indicators of various taxonomic units. Some types of bacteria have appropriate enzymatic systems that ensure the involvement of petroleum hydrocarbons in metabolic reactions, and as a result of their biodegradation. Researchers [7–9] proved the high efficiency of using the consortium of bacteria Aquimarina, Polaribacter, Salegentibacter, Sulfitobacter, Idiomarina, which have significant oil destructive ability at low temperatures, as well as other bacteria that play a key role in reducing the concentration of oil in water.

According to research [10] on average 80 % of fish biomass and 86 % of secondary fish production would be retained after partial removal, with above 90 % retention expected for both metrics on many platforms. Partial removal result in the loss of fish biomass and production for species typically found residing in the shallow portions of the platform structure.

When assessing the level of anthropogenic pressure on the Caspian marine ecosystem due to offshore oil production, one of the unresolved issues is the determination of the zone of active pollution or the zone of maximum impact. Today, models of Fei, Johansen and Elliot, Blocker and others are known for evaluating the spreading field of oil film on the water surface when oil is supplied in various quantities [11], but the influence of oil is only one component of technological risk.

The purpose of the paper is to comprehensively assess the oil production activities in the Caspian environment.

2 Research Methodology

2.1 Materials

When oil / oil products enter the sea, they form oil films, and those in turn are smoothing areas on the sea surface or slicks. At the beginning of the era of remote sensing of the ocean, all the spots-slicks on the sea surface and, accordingly, dark spots on radarlocation images (RLI) were considered as films of oil or oil products. In the first hours of film existence, physicochemical processes for the removal of petroleum hydrocarbons from the surface of water dominate [12]. Components with a low boiling point quickly evaporate, dragging fractions with a higher boiling point. In the first few days, depending on the composition of the oil and hydrometeorological conditions, 30–70 % of the oil is lost, mainly the C_4–C_{12} fraction. Chemical transformations of oil in the water column are oxidative, often accompanied by photochemical reactions under the influence of the ultraviolet part of the solar spectrum and can be catalyzed in the presence of certain trace elements, such as vanadium, and inhibited by sulfur compounds. The final oxidation products (hydroperoxides, phenols, carboxylic acids, ketones, aldehydes, etc.) usually have an increased solubility in water and are highly toxic. Photo-oxidative reactions initiate the polymerization and destruction of the most complex molecules in the composition of oil, increase its viscosity and the content of tar and asphaltene products and contribute to the formation of solid oil aggregates.

Films of crude oil and heavy oil products (including emulsions) are very thick and can reach a thickness of several millimeters on the sea surface, ranging in color from dark brown to metallic gray. Crude oil is capable of forming emulsions on the sea surface, which can contain up to 80 % of water (visually from light brown to orange). The shapes and sizes of the spots of oil and oil products are extremely diverse. These contaminants may appear near oil platforms, floating storage facilities, terminals, pipelines, wells, other operating or abandoned offshore oil and gas facilities; they are formed as a result of exploration, drilling, production, transportation and other operations with oil and oil products, as well as result of accidents with tankers and oil platforms. A significant part of oil and oil products can be carried with river runoff in cases where leaks and accidents occur on land.

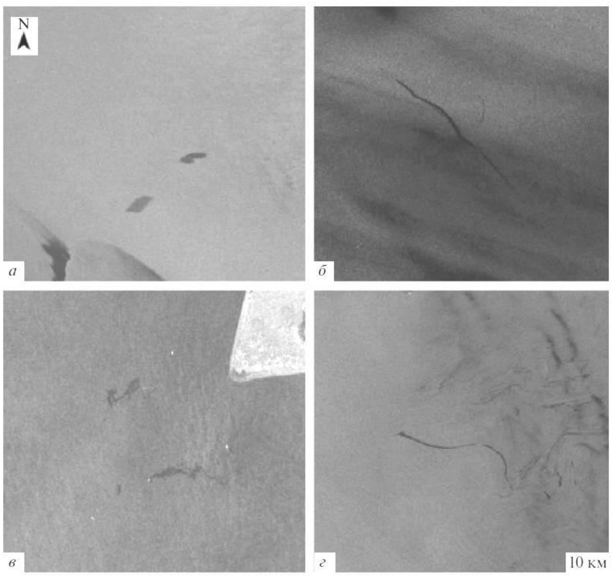

FIgure 2 – Examples of film pollution found in the Caspian Sea

Oil slicks glittering on the surface of the sea and thousands of hectares of soil penetrated by oil leaking from abandoned wells are just part of the pollution that people living around the Caspian Sea must endure. In addition there are various industries, particularly chemicals and mining, large-scale irrigated farming and untreated household waste. Combined with the effects of the oil, all these forms of pollution have a serious impact on the well-being of humans and wildlife.

Another source of oil products in the Caspian Sea is the industrial and economic flow of cities and towns along the coastal strip of the sea. 200 large cities with more than 220 sources of pollution of the water basin are concentrated in the Caspian region. Here, about 39 cubic kilometers of wastewater is discharged annually, of which almost 8 cubic kilometers are polluted. Together with sewage, up to 30 tons of petroleum hydrocarbons are dumped into the sea. Beyond the scope of statistical reporting, rainfall runoff of settlements, as well as emergency discharges [13].

2.2 Factors affected on the behavior and fate of petroleum compounds

Figure 3 shows the interrelationships among the physical, chemical, and biological processes that crude oil undergoes when introduced into the marine environment, subsequently weathers, and is then transported away from the source. Processes involved in the weathering of crude oil include evaporation, emulsification, and dissolution, whereas chemical processes focus on oxidation, particularly photooxidation. The principal biological process that affects crude oil in the marine environment is microbial oxidation.

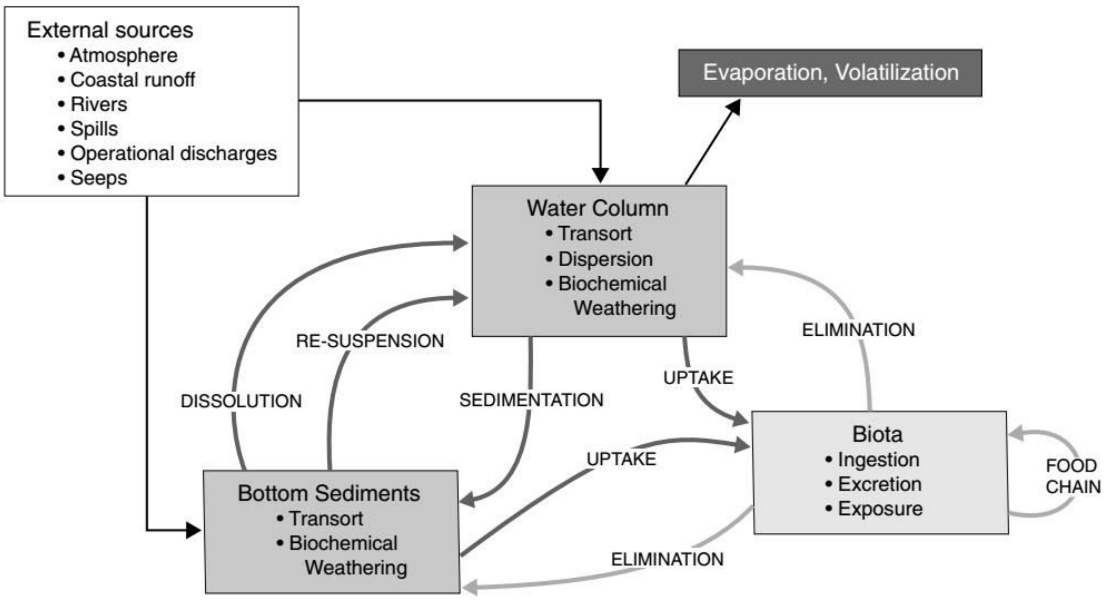

Figure 3 – Detailed interactions of a conceptual model for the fate of petroleum in the marine environment [14]

The kinetics of the breakdown of oil and petroleum products in the marine environment is determined by the influence of external factors related to the properties and characteristics of the environment in which the oil falls. Experiments have shown that the temperature factor is decisive in the kinetics of the breakdown of petroleum and petroleum products. In general cases, the rate of chemical reactions with a temperature increase of 10 °C increases by 2–4 times, and a decrease in the temperature of the medium significantly inhibits not only the physicochemical, but also the biochemical processes associated with the destruction and transformation of various substances. This is explained by the fact that temperature conditions have an undoubted effect on the rate of reproduction of the bacterial mass – as the temperature decreases, the total number and number of heterotrophic organisms decreases.

An increase in the salinity of seawater also adversely affects the biochemical oxidation of petroleum hydrocarbons. The changing of salinity by 1 % causes the half-life of petroleum hydrocarbons changes by 22 hours. However, for each marine region, changes in salinity are generally very small, and sharp salinity gradients are observed mainly in the zones of influence of river flow and melting (formation) of ice. The same can be said about the effect of pH on the biochemical oxidation of petroleum hydrocarbons. Thus, the effect of a change in the half-life of petroleum hydrocarbons on temperature is 25 times more than on changes in pH and 8 times more than on changes in salinity.

If the hardly soluble oil residues, together with the inorganic and organic impurities included in them, approach the density of sea water (or exceed it), then in this case they are sedimented. As a result, oil aggregates can sink to the bottom or leach onto the shore, which leads to the purification of the water column. In turn, the bottom sediments during wave roiling can be a source of pollution of marine waters.

2.3 Methods of mathematical modeling of the spreading of the oil film on the water surface

It is advisable to simulate the spreading of oil film to predict the scale of emergency oil spills in the sea, and as a consequence, the zone of maximum damage to the ecosystem. The process of spreading the oil film over the sea surface occurs under the action of various forces, but to simplify the task, we take into account the force of gravity and viscous friction. The main characteristics of the oil film will be its radius and thickness. The process is described using the mass conservation equation for the elemental volume of an oil film and the equation of motion of a viscous Newtonian fluid [15]. The equation of mass conservation for the mathematical model of the process under consideration in the axisymmetric case can be represented as

$$\frac{\partial h}{\partial t}+\frac{1}{r}\frac{\partial (ruh)}{\partial r}=0. \quad (1)$$

The equation of fluid motion is

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial r}=-g\delta\frac{\partial h}{\partial r}-\frac{\tau}{\rho_0 h}. \quad (2)$$

where h is oil film thickness, m; u is film speed averaged over film thickness, m/sec; τ is shear stress at the bottom of the film; g is acceleration of gravity, m/s^2; $\delta = (\rho_w - \rho_o)\rho_o^{-1}$; ρ_w, ρ_o is density of water and oil respectively, kg/m^3; r is radial coordinate; t is time, sec.

The solution of the differential equations (1) and (2) from the specified initial conditions by analytical methods allowed us to obtain a formula for determining the final radius $r_k(t)$ of the oil film at a certain point in time as the ratio

$$r_k(t)=\xi_0\left(\frac{V_0^3\alpha t}{8\pi^3}\right)^{1/8}. \quad (3)$$

Oil spill modeling is based on GIS technology. Modeling is done using software ArcGIS for Desktop Advanced v.10.2 and ADIOS® (Automated Data Inquiry for Oil Spills) is NOAA's oil weathering model. It's an oil spill response tool that models how different types of oil weather (undergo physical and chemical changes) in the marine environment. Working from a database of more than a thousand different crude oils and refined products, ADIOS quickly estimates the expected characteristics and behaviour of spilled oil.

2.4 Methods to assess impact concentrations of chemicals

The greatest source of uncertainties in deriving assessment end points (e.g. a PNEC; the concentration below which organisms in the area of interest are unlikely to be adversely affected) is the extrapolation of laboratory bioassay results to the natural environment. The requirement to both culture and maintain test species in the laboratory restricts the selection of possible test species and the species used are often not very representative for the large spectrum of species, with varying degree of sensitivity that may occur in natural ecosystems. This exercise of extrapolation therefore involves many often untested assumptions (Figure 4).

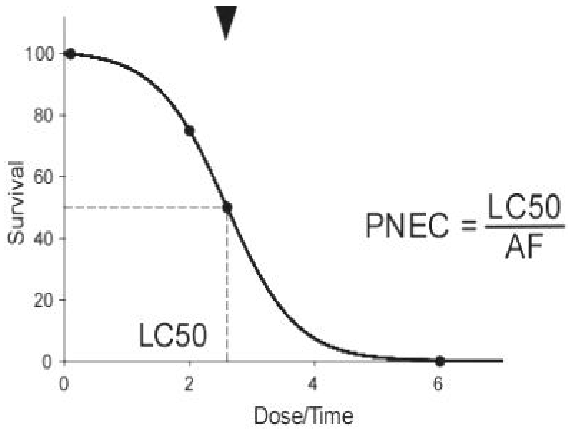

Figure 4 – Dose-response relationship based on laboratory toxicity test (bioassay), here fish

The outcome is often that the PNECs may be either overprotective or underprotective, depending upon the biological and environmental conditions that apply at each natural site [16, 17]. This severely limits the usefulness of the chemical criteria in Ecotoxicological Risk Assessment (ERA). The two main approaches used to extrapolate lab data to field data to obtain an estimate of the field Predicted No Effect Concentration (PNEC) is (1) using an assessment factor approach or, when sufficient data are available, (2) from statistical extrapolation.

LC50 is the lethal concentration to 50 % of the individuals but any level of biological organization (e.g. molecular, cellular, organ and organism), effect level (e.g. NOEC, the highest concentrations with no observed effect and LOEC, the lowest concentration with observed effect) and life history variable (growth, reproduction, swimming speed etc.) can be used to estimate an effect concentration.

Experience shows that different species differ in their sensitivity towards a single chemical. This may be due to differences in life history, physiology, morphology and behavior. The species sensitivity distributions (SSDs) approach is a statistical description of the variation among a set of species in toxicity of a certain compound or mixture (Figure 5). SSDs consider variation between species and not within species and do not attempt to explain why species differ in sensitivity. It is a probabilistic approach in contrast to the deterministic procedure of assessment factors.

As mentioned [18] forward use ($x \rightarrow y$) in risk assessment and inverse use ($y \rightarrow x$) in EQC is indicated.

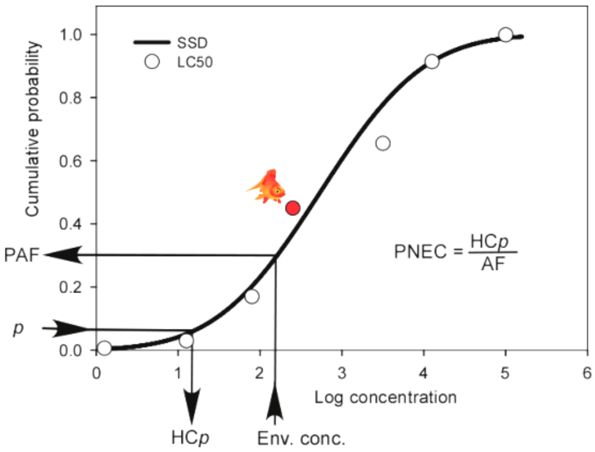

Figure 5 – Species sensitivity distribution combining results from various single species bioassay

2.5 Methodology of oil toxicity studies

Under the Chemical Response to Oil Spills: Ecological Research Forum (CROSERF) [19] is often used to determine lethal concentrations. In general, field studies allow for less control of environmental variables but allow for investigations that may not be possible in most laboratory experiments (e.g., multi-species assemblages). Field experiments are also more costly and regulatory approvals from various stakeholders are sometimes difficult to obtain.

Multivariate analysis and the biotic index (BIOSTRESS) Multivariate analysis is regarded as the most sensitive technique for distinguishing site groupings of disturbed assemblages related to oil activity. Subtle effects induced by pollutants may be reflected in changes in the community composition that may be identified using the biological criteria discussed above (e.g. similarity matrixes, species response models) together with multivariate techniques (e. g. ordination and classification) [20].

3 Results

Studies on natural models in the Caspian Sea have shown that physicochemical oxidation plays a significant role in the breakdown of petroleum hydrocarbons, which is consistent with the results of the practical development of a system for protecting the biological diversity of the Caspian Sea from oil pollution [22].

A summary of the processes that affect the fate of petroleum hydrocarbons from seven major input categories is shown in table 1. Each input is ranked using a scale of high, medium, and low that indicates the relative importance of each process. The table is intended only to convey variability and is based on many assumptions.

Table 1 – Processes that move petroleum hydrocarbons away from point of origin

Input Type	Seeps	Spills	Light distillates	Crudes	Heavy distillates	Produced water	Vessel operational	Atmospheric
Persistence	years	days	days	months	years	days	months	days
Horizontal Transport or Movement	H	L	M	M	H	L	M	H
Vertical Transport or Movement	M	NR	L	M	H	L	L	NR
Evaporation	H	H	M	M	L	M	M	H
Emulsification	M	NR	L	M	M	NR	L	NR
Dissolution	M	M	H	M	L	M	M	M
Oxidation	M	L	L	M	L	M	L	M
Sedimentation	M	NR	L	M	H	L	L	NR

Note: H = high; L = low; M = moderate; NR = not relevant.

The resulting (integral) film pollution maps found in the Northern Caspian in 2009–2013, 2014–2015, are shown in Figures 6 a, b. For the convenience and simplicity of the analysis on these maps the boundaries of state sectors (economy zones), the main ship routes and license areas are plotted. They were created by combining all the vector contours of the found pollution for one year into one layer and then merging the annual maps into one.

National Caspian Action Plan of Azerbaijan, 2002; National Action Programme on Enhancement of the Environment of the Caspian Sea, Kazakhstan 2003–2012; Environmental Performance Review of Kazakhstan, UNECE, 2000; Environmental Performance Review of Azerbaijan, UNECE, 2003; Study for; Safe Management of Radioactive Sites in Turkmenistan, NATO, 2005; Environment and Security: Transforming Risks into Cooperation, Case of Central Asia, 2003 ; Global Alarm: Dust and Sandstorms from the World´s Drylands, UNCCD, 2001.

The concentration of SPAR in the water area was higher when it was calm (0.45 mg/l) than under the conditions of the northern (0.31 mg/l), southern (0.26 mg/l), western (0.23 mg/l) and east (0.13 mg/l) winds [22]. Moreover, the content of oil components in the west (0.34 mg/l) of the region always exceeded their indicators in its eastern and central (0.14 mg/l) parts. The NU content in the water area decreased from weak (0.15–0.32 mg/l) to moderate (0.09–0.24 mg/l), significant (0.07–0.19 mg/l), and severe disturbances. The effect of the latter in calm is also combined with a decrease in the oil content in the range (0.09–0.27 mg/l). Integrated map of film pollution is shown in Figure 6.

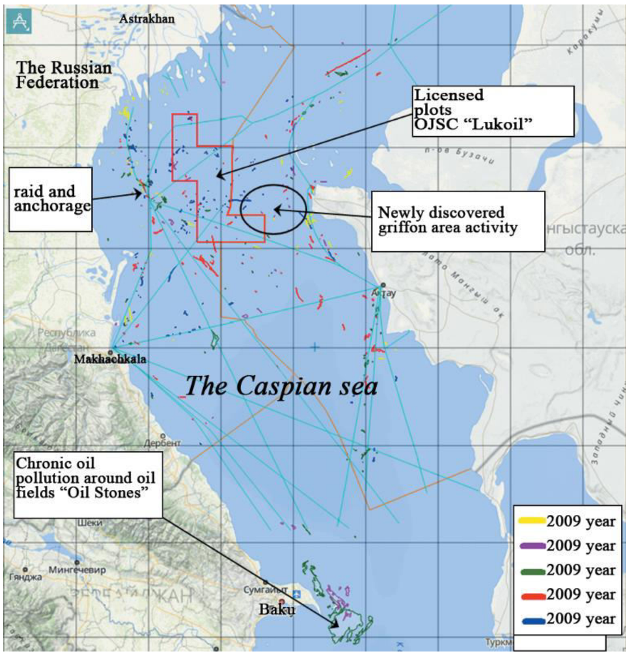

Figure 6 – Integrated map of film pollution found in the Caspian Sea in 2009–2013: light brown lines are the boundaries of public sectors, blue ones are the main ship routes; red is licensed blocks of OAO "Lukoil"

4 Discussion

In the northern part of the Caspian Sea, where oil is being actively extracted, no films of crude oil were found (Figures 6 a, b). This, in general, is explained by effective industrial and environmental safety measures that Lukoil uses during exploration and production of oil in the Caspian Sea. (According to company representatives, the risk of emissions of crude oil is virtually zero.) 6a shows a map of the distribution of film contamination in the sea for 5 years, from which it follows that the largest pollution areas were found in the main shipping routes and approaches to the Caspian ports of Russia and Kazakhstan. They are also ship-based and can be mining, bilge water and other liquid waste, due to commercial transport and fishing, and, to some extent, tanker shipments of oil. This is also confirmed by rice, and Figure 6 b is for 2014–2015.

The results of experiments in the Caspian Sea showed that lowering the temperature of the aquatic environment by 10 °C lengthens the half-life of dissolved forms of oil by 2 times, and a change in the temperature of the medium by 1 °C changes this period by 40 hours. Thus, with a decrease in water temperature from 28 °C to 0 °C, the half-life period is extended by 1.12 hours.

The wind speed is important for the spread of oil spills on the surface of the Northern Caspian, along with the direction. With its increase in the area of water there is a decrease in the concentration of oil impurities from weak (0.15–0.32 mg/l) to moderate (0.08–0.18 mg/l) and strong (0.07–0.15 mg/l) winds [23]. However, in the case of continuous operation of the source of pollution with the same wind, the amount of petroleum hydrocarbons first decreases and then increases again, stabilizing at the original level.

The inertia of levels of sea pollution associated with the action of winds is noted. With the duration and constancy of the volumes and the quality of the anthropogenic runoff, after some decline, the concentration of toxicants is restored. At the same time, the dual role of winds and waves in self-purification and secondary pollution of sea waters as a result of their mixing and stirring up of bottom sediments can be traced. Other things being equal (distance from the source of pollution, depth of occurrence, physical properties) the content of harmful impurities in bottom soils depends on the degree of their dispersion, the predominance of fine or coarse fractions.

Despite the relatively small losses of hydrocarbons during their production on the shelf, emergencies at drilling rigs remain inevitable so far, and with emergency and technological discharges of oil products into the sea from drilling rigs, pollution is mostly local in nature. However, near the source, the concentration of petroleum hydrocarbons may be tens or hundreds of times higher than the norm established for fishery bodies of water. On average, during the development of fields, 30–120 tons of oil comes from a single well into the marine environment. In cases where local pollution becomes chronic, oil not only pollutes water, but also bottom sediments.

Studies have revealed the dependence of the toxic effects of wastewater, drilling mud and sludge on the organisms of the Caspian Sea on their composition and habitat conditions. Oil hydrocarbons at a concentration of 0.05–0.5 mg/l, as a rule, do not affect the survival of marine organisms if their toxic effect is not aggravated by the action of other toxicants. At the same time, almost all tissues and organs show physiological and biochemical changes that become irreversible with an increase in the concentration of oil from 0.5 mg/l to 50 mg/l. Already at the very bottom of this interval (0.5–1.0 mg/l), changes in physiological and biochemical parameters are accompanied by impaired growth and development, as well as fish fertility. Reduced fertility is manifested to a greater extent in subsequent generations. The stability of aquatic and benthic organisms to the toxic effects of oil depends on their taxonomic identity and stage of development, the concentration of hydrocarbons, the duration of exposure, and its combination with other factors and environmental conditions.

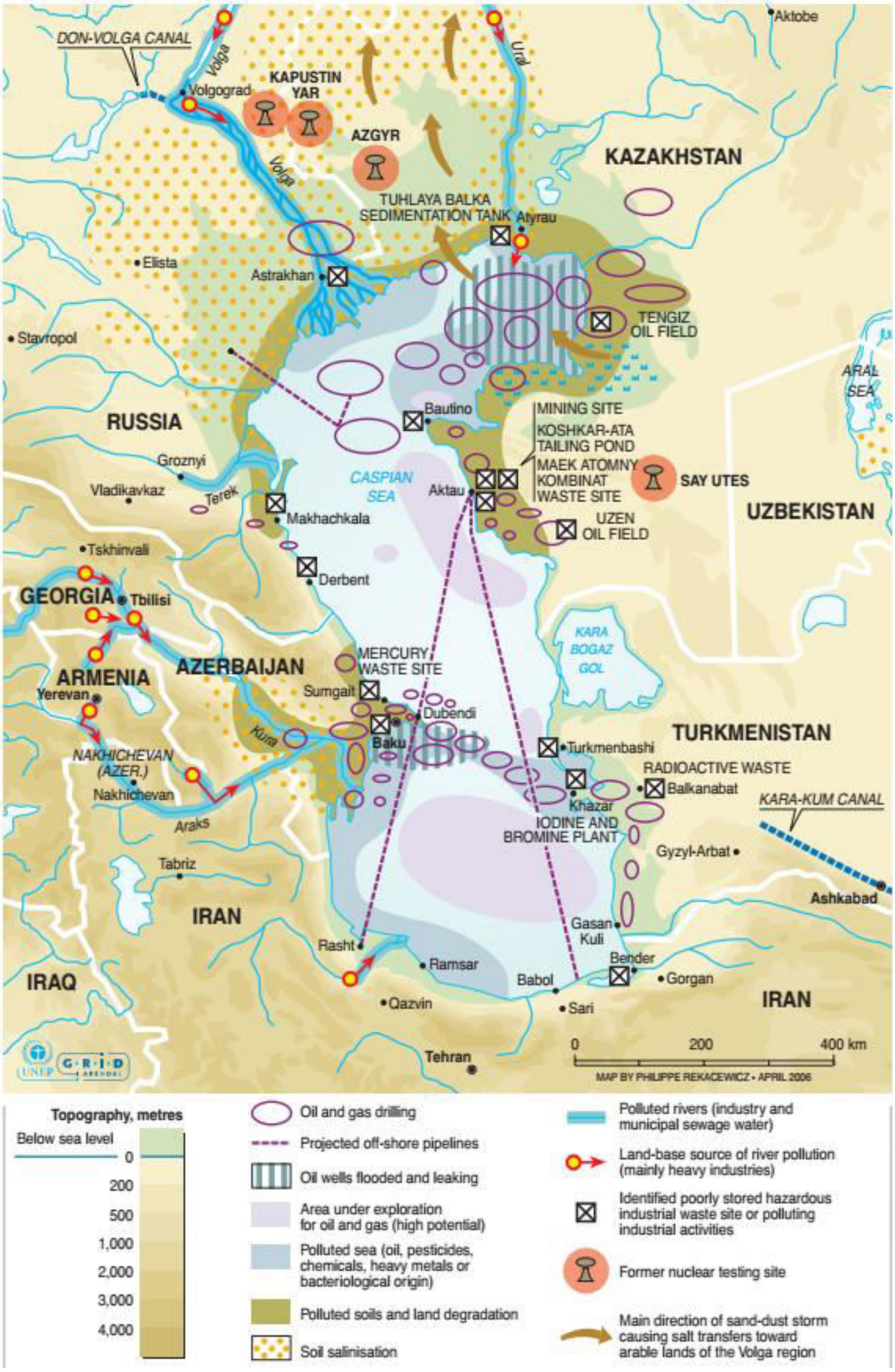

Figure 7 – Hazards in and around the Caspian

5 Conclusions

The ecological state of the Caspian Sea is deteriorating due to the intensification of oil production on the sea shelf. The influx of petroleum hydrocarbons into the aquatic environment occurs additionally due to river flow. It is determined that the components of oil undergo transformations under the influence of physical, chemical and biological processes. Under the conditions of temperature, salt and wind regimes characteristic of the Caspian, these reactions are based on photo-oxidation processes. Nevertheless, biodegradation plays an important role. Analyzed models of spreading oil film, allowing to determine and predict contaminated areas. The main ways of xenobiotic influence on hydrobionts are considered.

According to the results of the assessment of the technogenic load on the natural environment of the Caspian Sea, zones of high, moderate and low levels of environmental risk were identified (Figure 7).

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Аналіз техногенного навантаження від нафто-газової промисловості на Каспійський регіон

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Анотація. Проблема інтенсивного забруднення Каспійського моря продовжує залишатися однією з найважливіших і найсерйозніших для регіону. Особливе занепокоєння викликає підвищення рівня забруднення нафтовими вуглеводнями узбережжя Каспійського моря. Мета даної статті полягає в оцінці ступеня забруднення прибережної зони Каспію нафтовими вуглеводнями. Авторська ідея полягає у забезпеченні комплексного аналізу екодеструктивних факторів процесу нафтового видобутку на природні комплекси, зокрема впливу хімічного забруднення нафтовими вуглеводнями водного басейну на місцеві гідробіонти. У роботі використані методи математичного моделювання поширення нафтових плівок на поверхні води, спрямовані на прогнозування області впливу, а також методи токсикологічних досліджень та оцінювання взаємозв’язку «доза – ефект». Встановлено, що води Каспійського моря, пов’язані з видобутком нафти, є районами підвищеного екологічного ризику. У випадках, коли концентрація вуглеводнів перевищує 1 мг/л, фізіологічні зміни спостерігаються у більшості домінуючих груп гідробіонтів. Зони підвищеного рівня ризику для морських екосистем, спричинені розвитком газової та нафтової промисловості, пов’язані з північною та південно-західною частинами Каспійського моря. На підставі проведених досліджень одержані результати, необхідні для розроблення програм забезпечення екологічної безпеки досліджуваного регіону.

Ключові слова: нафтове забруднення, видобуток нафти на морському шельфі, гідробіонти, екологічний ризик, витоки, Каспійський регіон, нафтова плівка, оцінювання ризиків, біодеградація, математичне моделювання.