Oil and Gas Development on the Sakhalin Island Shelf: An Assessment of Changes in the Okhotsk Sea Ecosystem

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The vast amount of oil and gas deposits on the Sakhalin Island Shelf has been surveyed intensively over the last twenty years. Many large companies (Marathon, Shell, Exxon, Sodeco and others) have already completed preliminary plans on oil and gas production on the eastern and north-eastern sites of the Sakhalin Island Shelf within the framework of the Sakhalin-1 and Sakhalin-2 projects. The stocks of just one of the five surveyed deposits (Odoptinskii) amount to more than 200 million tons of oil and 10^{11} cubic meters of gas [1]. The total amount of oil and gas on the north-eastern shelf of Sakhalin Island is 1.2 billions ton and 800 billion cubic meters respectively [2].

Under the proposed Sakhalin-1 project, Sakhalin Island will become a large oil and gas extracting center and supplier to the Far East and abroad. 65 prospecting wells have been drilled on the Sakhalin Island Shelf [3]. The project calls for the construction of six drilling platforms (one self-elevating), the drilling of more than 600 wells (up to 3000 meters deep) producing more than 60,000 tons of oil and 80 million cubic meters of gas per day, the laying of a system of underwater pipelines (with a diameter of up to 720 mm), the building of large shore facilities, and the removal of up to 70,000 cubic meters of the seabed [4].

This paper will analyze the impact of the modern marine oil and gas industry on a marine environment and fisheries in marine shelf and oceanic zones. The extraction of oil and gas in a marine environment has been a sector of the global economy for the last 20 years. This paper will examine the negative impact of this industry on marine ecosystems and biological resources. It will determine the degree of damage caused by water pollution and changes in fishery conditions in regions where oil and gas extraction has occurred. It will formulate the steps necessary for preserving the environment in regions of oil and gas extraction.

The Environmental Effects of Marine Shelf Oil and Gas Extraction

There are many examples of humanity's negative impact on water ecosystems, such as the discharge of industrial wastes, the washout from fertilizers, toxic chemical dumping, the damming of rivers, and unsustainable water consumption. The large-scale development of marine shelf oil and gas deposits has also had a negative impact. The technology for oil and gas recovery used in Russia for land-based continental deposits is combined with ecological risk owing to significant losses of extracted raw materials.

The most widespread and dangerous consequence of marine oil and gas (as well as any other) industry is pollution of the environment [5]. Pollution is associated with all kinds of activities at all stages of a deposit's development. Globally, the oil and gas industry disposes of more than 3 billion tons of solid wastes, about 500 km^3 of sewage and about 1 billion tons of aerosols per year [6, 7]. These releases are composed of more than 800 substances, many of them related to oil and its by-products. Globally, the total annual loss of oil during its production and transport exceeds 45 million tons; 22 million tons are lost on land; about 7 million tons are lost in the sea; and 16 million tons enter into the atmosphere as a result of the incomplete combustion of liquid fuel [7]. The essential part (up to 10 to 20%) of the total volume of marine gas production is burned up in flare systems and gas generators on platforms and is a source of atmospheric pollution.

Practically all stages in the development and production of hydrocarbons are accompanied by discharges of liquid, solid and gaseous waste (Table 1). The typical discharge volumes of the most widespread and hazardous substances are shown in Table 2.

There are four main stages in the development of oil and gas deposits [1]:

1. geological and geophysical surveys and evaluation of raw material stocks (seismic and drill exploring);
2. the preparation of a deposit for exploitation (installing stationary platforms, laying pipelines, constructing shore terminals, drilling works, testing wells, etc.);
3. the deposit's exploitation (extraction, separation and primary processing of hydrocarbons; the sinking and reparation of wells; the transportation of liquid and gaseous products, etc.);
4. completion and termination (dismantling work; the removal of platforms and pipelines; the preservation of wells, etc.).

Each of these stages is characterized by certain activities and has an influence on the environment (Tables 3 and 4). This influence has a complex character and is seen in the form of the physical, chemical and biological effects in an aquatic environment, the seabed bottom and, partially, in the atmosphere.

The mean time of a deposit's exploitation is 20 to 40 years. However, after only 5 to 10 years, an area may have new petroleum platforms, abandoned drill constructions, different devices for laying underwater pipelines, oil tankers, vessels for seismic investigation, etc. Thus, the local effects are integrated and become regional. Their character and intensity can be distinguished depending on the combination and number of natural and technical factors. For example, in the North Sea, there are around 4000 drill wells (160 are working from stationary platforms), and about 250 underwater terminated wells and more than 5000 km of underwater pipelines [13].

The development of any oil field results in the release of polluting substances into the atmosphere. As for the development of marine deposits, this fact has not attracted special attention so far. However, oil and gas recovery experience on land shows that releases into the atmosphere occur at all stages of development. The most widespread sources of such releases are [1]:

- the continuous or periodic combustion of gas and excessive quantities of hydrocarbons during the testing and operation of wells and the continuous combustion of flares and low pressure ignition devices for gas removal from tanks and pressure regulation systems;
- the combustion of gaseous and liquid fuel in power equipment (gas turbines, internal combustion engines) on platforms, vessels, and shore structures;
- the releases from degasified drill solutions, technological reagents and extracted hydrocarbons used in various operations for production, processing, transportation and storage .

The volumes of annually combusted petroleum gas in Russia amount to 10 to 17 billion cubic meters [14]. Preliminary calculations for Great Britain's marine oil and gas industry have shown that about 10% of produced gas (approximately 46 billion cubic meters) is combusted in flare systems and used for its own oil field power requirements [15]. The total amount of releases resulting from the production of oil and gas in Great Britain's sector of the North Sea are estimated at 20,000 tons annually; the emission of methane is about 75,000 tons annually (or accordingly, less than 0.02 and 0.08% of all atmospheric releases of volatile organic compounds in Great Britain). Similar assessments for marine oil and gas fields on the Norwegian Shelf showed the dominance of carbon dioxide gas (88%) in atmospheric releases as well as nitrogen oxides and volatile organic substances [16].

Deposit waters entering from underground oil and gas bearing structures during the industrial extraction of hydrocarbons account for a large amount of pollution. In some cases, the additional disposal of large volumes of marine water (tens or even hundreds of thousands of tons) is primarily pumped through forced channels to maintain well pressure. These waters are usually polluted by oil, low-molecular hydrocarbons, inorganic salts, technological reagents and suspended substances and should be treated before disposal into the sea. Such treatment in marine conditions, however, is technologically hindered [17].

Data from the 1980s for British oil and gas fields in the North Sea show that 60 to 78% of all usable chemical materials were disposed as wastes into the sea (or annually 117,000 to 138,000 tons) [15].

The volume of drill wastes is usually within 1000 to 5000 cubic meters per each passed well, and their amount is usually measured by tens (for one commercial platform) and many hundreds of thousands of cubic meters (for larger deposits). In the North Sea, 22,000 tons of oil, 100,000 tons of chemical admixtures (inorganic and low toxic), and 4900 tons of potentially dangerous compounds (biocides, corrosion inhibitors, detergents, demulsifiers, oxygen absorbents, etc.) entered the water with drill slime disposals in 1988 [18].

At present, two main types of drill solutions are used - mixtures based on oil and other organic substances (diesel fuel, paraffins and others) or water (fresh or salt with the addition of clay and other components). During the last 10 years, the preference has been given to the least toxic water-based drill solutions. However, in some cases (for example, in the drilling of inclined wells in solid rock) oil-based solutions are used [5].

Accidents remain inevitable events for any oil field. As well, they are a pollution source at all stages of the industrial exploitation of oil and gas deposits (during prospecting drilling, industrial production, and transportation by pipeline and oil tankers). The most prevalent reasons for accidents are: equipment failures, staff errors and extreme natural phenomena (seismic activity, glacial fields, storms, etc.). The ecological consequences of accidents are especially dangerous near the coast, in shallow water or in the areas with slow water exchange [1].

One of the main factors behind ecological risk in marine oil fields is the failure of underwater pipelines. The reasons for their damage can be quite varied (from material defects and pipe corrosion, up to ground erosion, tectonic shifts in the seabed, and effects of ship anchors and bottom trawls). The evaluated mean probability of accidents with underwater pipelines in North America and Western Europe is 0.00093 and 0.00064 respectively, and the main cause for these failures is welding defects [4].

The Russian experience in the development of oil fields in Siberia shows that the oil outflow from pipelines is a common phenomenon: 1 to 2% of the oil extracted in Russia is lost as a result of accidental spills and releases. The amount of these losses (for example, in the Tumen' area in Komi Republic) is estimated in the hundreds and thousands of events, and the volume of oil spilled is estimated in the millions of tons [19, 20]. If this rate of loss is repeated in oil and gas deposit development on the Sakhalin Island Shelf, serious consequences will occur. The construction of a main pipeline is planned along a greater part of the eastern coast of Sakhalin Island and through main rivers where the spawning and the reproduction of unique salmon populations occurs. On the whole, the construction of oil pipelines threatens to pollute rivers and lakes, as well as soils and underground water resources [21].

Despite the increased attention to ecological safety and accident prevention in marine oil fields, emergencies are inevitable. Statistics show that on the American shelf of the Gulf of Mexico, the number of emergency oil spills (in volumes of more than 1000 barrel (one barrel = 134 kg) per billion barrels of oil extracted or displaced averages 0.79 (during drill work on platforms); 1.82 (during oil transportation by pipelines) and 3.87 (during transportation by tankers) [22]. The volume of oil spilled during failures at drill works on the Great Britain Shelf in the period from 1980 to 1988 were between 0.00011 and 0.0029% of the amount of annually extracted oil on similar drill platforms [23].

The probability of accidents occurring on drilling wells is 0.1 to 0.5%, and, during their repair, 1 to 2.5% [24]. In cases of larger oil spills (more than 10,000 tons), emergencies do not exceed 3% [4]. Available studies show that 2.3% of the total number of marine drill platforms experience large failures annually [25]. Oil spills on a surface may be easily noticed and handled. However, about 33% of reported releases from marine wells were in the form of natural gas in the shallow-water areas of a shelf, and about half of these cases were connected with the serious failure and damage of drill installations [26].

The ecological consequences of oil tanker transportation and failure statistics are considered in detail in many publications [9, 27-29]. The probability of tanker accident (more than 10,000 tons of tonnage) is evaluated as 2.3% for each 10 million tons of deadweight. In other data, the specific accident rate of oil tankers with tonnage more than 6000 tons was around 2% at the end of the 1980s [30].

Running aground on coastal reefs, collisions with other ships, and fires and explosions of cargo are often mentioned as the main reasons for tanker accidents and other large oil spills. In 1989, the amount of oil spilled in tanker accidents was 114,000 tons; in 1990, 45,000 tons. The total annual volume of pollution from marine oil transportation is more than 500,000 tons [27].

Many examples are available in literature and statistics on large tanker accidents (about 2% per year) which clearly illustrate the high risk of emergencies during hydrocarbon transportation in the Barents Sea. They also testify about the possible catastrophic consequences of accidents because the damage can exceed all recorded cases. Calculations confirm the validity of this fear: for oil tankers with a tonnage between 5000 to 50,000 tons the area of oil and gas condensate spills could be between 3000 to 50,000 square kilometers; for super-tankers, spills could reach up to 84,000 square kilometers [31]. This would have a devastating effect on fisheries.

An examination of large tanker accidents, covered in detail in literature, begins with the *Torrey Canyon* tanker accident near the English Channel in 1967, when a spill of 95,000 tons of oil polluted the Atlantic coast of France and England with many consequences to the environment and fisheries. Many other accidents, such as the *Amoco Cadiz* (1978, 220,000 tons of oil), the *Exxon Valdez* (1989, 40,000 tons of oil), the *Braer* (1993, 85,000 tons of oil) have followed. Each of these accidents had its own causes, but in all cases the level of petroleum pollution reached lethal or threshold concentrations for marine fauna (especially for birds and mammals), with consequences far beyond ecological damage to the sea and the coast [1].

Regarding the scale and burden of the consequences that followed after the *Exxon Valdez*, the costs of the clean-up were 2 billion dollars; compensation for the environmental damage and to the local population was above 3.5 billion dollars. About 15 billion dollars should be added to these costs for judicial procedures [32].

Other dangerous situations can arise with gas-carrier ships, which are used alongside with oil tankers for the transportation of liquefied natural gas. Such accidents are less probable in comparison with oil tanker spills, but they threaten the destruction of all forms of life in an area up to 400 square kilometers [29]. Of seven gas carrier ship accidents (recorded until 1980) transporting liquefied natural gas, three cases were caused by explosions.

An accident with a ship transporting methanol (a toxic substance completely dissolvable in water) may lead to an ecological tragedy. Calculations have shown that an accident involving a similar ship with a tonnage of 35,000 tons, for example, in a coastal zone in the western part of the Murmansk area would destroy thousands of square kilometers of fisheries [31].

Composition of Oil in a Marine Environment and Sediment

At the end of the 1970s, an international project to monitor petroleum pollution was carried out [33, 34]. Data from visual observations (about 100,000) and chemical analyses of marine water samples (several thousands) from all regions of the world's oceans were analyzed. The presence of dissolved and emulsified oil hydrocarbons in surface waters in concentrations of up to several μg/l (and in regions of increased petroleum pollution - up to several mg/l) was revealed everywhere. Many instances of floating petroleum aggregates and petroleum films (slicks), which covered 0.5% of surveyed oceanic surfaces, were found [35].

Generally, increased concentrations of oil pollution were found in the bottom sediments of river mouths and deltas, estuaries, bays, inlets, ports and in regions used for navigation, extraction and transportation of oil [1].

During the last 10 to 15 years, there has been a decrease in the severity of marine pollution as a result of stricter international rules for the disposal of oil-containing ship sewage and ballast waters of oil tankers. However, marine environment pollution by oil products remains a serious threat. In this environment, highly toxic water-soluble particles of oil products dispersed as separate "drops" are present.

According to observations made in 1993 in the Okhotsk Sea, the average concentration of dissolved aliphatic hydrocarbons (DAH) and polycyclic aromatic hydrocarbons (PAH) varied in the range of 15 to 33 μg/l and 5 to 12 ng/l respectively. In bottom waters, the content of aliphatic hydrocarbons in suspended substances reached 68% of its total mean value. The background value of DAH in the Okhotsk Sea was accepted at about 20 μg/l. In the north-eastern part of the Sakhalin Island Shelf, the mean content of DAH was

10 times higher (202 μg/l) and in certain cases reached 2172 μg/l owing to local petroleum pollution in the region. The increased content of oil hydrocarbons in the marine water of this region is related to natural infiltration from sedimentary rocks. Structural analysis of the permeating DAH showed their strong similarity to crude oil in the sediment [36].

Mean and maximum concentrations of oil hydrocarbons in bottom sediments of the northeastern part of the Sakhalin Island Shelf were 0.08 and 0.18 mg/(g dry weight) respectively, and these values were higher than in waters off the Kamchatka Peninsula Shelf and in coastal sediments of the Pacific Ocean [37].

The distribution of oil hydrocarbons may vary in regions influenced by the local inputs of the oil. The content of oil substances in the surface micro-layer always exceeds (up to 10 times and higher) their content in the water column. In the surface water micro-layer of the northeastern part of the Sakhalin Island Shelf, the concentrations of DAH and PAH were on average 0.574 mg/l and 5032 ng/l respectively [36].

The Toxic Influence of Oil and Its Products on Marine Flora and Fauna

Oil and its products belong to a group of toxicants made up of complex structures that have various effects on living organisms from physiological damage up to cancerous effects. In the literature on marine toxicology, there are many studies related to questions on the degree of biological danger from oil pollution ranging from studies which report an absence of harmful effects (in water with an oil concentration of approximately several mg/l), to studies which show damage to the vitality of aquatic organisms even in the presence of small amounts of dissolved oil hydrocarbons (in the hundredth and thousandth parts per mg/l) [9, 28,38-43], and oil-spill dispersants [44]. Different opinions may also be found on the ecological consequences of oil spills and the influence of low concentrations of chronic oil pollution on aquatic organisms [35, 45-49]. The reaction of marine biota (algae, macrophytes, crustaceans, mollusks, benthos, fish) even to low concentrations of oil hydrocarbons (< 0.001 - 1 mg/l) in marine water is rather diverse, and on the whole, a decrease in the population and mortality aquatic organisms has been demonstrated [1, 50].

One method of assessing the toxic influence on aquatic organisms is based on the LC50 determination (or a substance concentration causing the death of 50% of the number of organisms in experiments with a duration of 24 to 96 hours). In the majority of experiments conducted, the values of LC50 for different types of drill solutions were within the range of 10 to 100 g/kg which corresponds to their dilution of 1 to 10%. The exception is made for drill solutions prepared on the basis of diesel fuel for which the LC50 value is much lower and can reach the threshold value 0.1 g/kg. This has formed the basis for the limitation (and sometimes prohibition) in the use of oil-based drill solutions and their gradual replacement by water-based ones and other solutions (without including oil and other toxic substances in their structure).

Some ideas about the LC50 values of dissolved hydrocarbons for aquatic organisms and the correlation of this parameter with the size of biota may be found in Fig. 1 and 2: they show the general tendency of increasing the sensitivity and vulnerability of small-sized forms of aquatic organisms (including the embryonic and larval growth stages) to the presence of toxic admixtures (namely oil hydrocarbons).

There are a wide range of toxic and threshold concentrations of dissolved oil (mainly hydrocarbons) for investigated aquatic organisms (Fig. 3). The increased sensitivity to the presence of oil is found in the majority of investigated fish [51] and invertebrates in the early stages of their growth. The toxic concentration which causes the destruction of organisms or irreversible damage to vitally important functions, for caviar (embryo), larvae and fingerlings of marine animals is usually much lower than for adults and reaches minimum values of 0.01 to 0.1 mg/l.

Benthos and demersal forms (including many kinds of fish living in constant contact with the polluted sediments) are especially vulnerable. The bottom fish show tumors, mutations and diseases of cancerous character when the concentration of some DAH in sediments is in the range of 3 to 5 mg/kg or higher.

The maximum value of harmless concentrations of dissolved oil hydrocarbons is about 0.001 mg/l. These concentrations are usually found in waters remote from the coast, in pelagic regions of oceans and seas, not subject to the effects of oil pollution.

Oil concentrations in the 0.001 to 0.01 mg/l range can be viewed as a zone of reversible threshold effects. These concentrations are found in relatively clean pelagic and coastal waters. The possible primary (basically physiological and biochemical) reaction of biota to similar concentrations is evidence of the presence of oil hydrocarbons. The permissible content of oil hydrocarbons in marine water is just in this range [1].

Higher concentrations of oil products (0.01 to 1 and above 1 mg/l) result in sublethal and lethal effects. They may be found in bays, estuaries, port harbors and bays with slow water exchange and increased concentrations of chronic oil pollution, as well as in areas with emergency spills of the oil, sewage discharges, etc.

The ranges of toxic and threshold concentrations of oil products are shown in Fig. 4 for organisms inhabiting sediments.

The Composition of Oil Components in a Marine Environment

From the chemical point of view, oil is a complex mixture of several thousand hydrocarbons (basically liquid, accounting for 80 to 90% of the mass) with a mixture of derivatives containing sulfur (mercaptans, thiophenes, disulfides, thiophanes and others), nitrogen (homologues of pyridine, acridine, hydroquinol and others) and oxygen (naphthenic acids, asphaltites, resins and others). Crude oil also contains water (up to 10%), dissolved hydrocarbon gases (up to 4%), mineral salts (mainly, chlorides - up to 4 g/l) and many microelements whose concentration ratios (more often vanadium and nickel) serve as additional characteristics regarding the origin and properties of oil. Four groups of compounds are usually allocated among oil hydrocarbons [1]:

1. alkanes - paraffin (acyclic) saturated hydrocarbons with direct or branched chains of C atoms (40 to 50% of volume);
2. naphthenes (cycloparaffins) - saturated cyclic and polycyclic compounds in which H atoms may be replaced by alkyl groups (25 to 75%);
3. arenes - aromatic unsaturated cyclic compounds from the benzene order where the H atoms may be also replaced by alkyl groups (usually up to 10 to 20%, rarely up to 35%);
4. alkenes (olefins) - unsaturated acyclic hydrocarbons with direct or branched chains and double connection C=C (the compounds of this group are not part of crude oil but are the main product of its cracking).

Oil's properties are exhitibted in their ability to exist in a water environment in several aggregate states: surface films (slicks); dissolved forms; emulsions ("oil in water" and "water in oil" type); suspended forms (black oil aggregates floating on the surface and in water mass, oil fractions absorbed in particulates); solid and sticky components settled at the bottom; compounds accumulated in aquatic organisms.

Long-term observations in the Baltic Sea showed that 3.6% of the total amount of the oil is in the film state, 0.4% is adsorbed as rough suspension, 15% is accumulated in bottom sediments, 64% is emulsified, and 17% is found in a dissolved state [52].

Oil and oil products flowing in water rapidly cease to exist in the initial substrate. Their fate and biological action in water ecosystems are determined by natural and physiochemical properties, mainly by volatility (vapor pressure), gravity and solubility in the water. Almost all components of crude oil and its fractions have a density less than 1 g/cm^3, and the majority of them may be dissolved to a certain degree. Simultaneously, the evaporation of easily volatile fractions takes place.

In conditions of chronic oil pollution, emulsified oil is frequently the dominant oil fraction. It is determined by the action of hydrodynamic factors (wind patterns and others) and by the prevailing method of oil entry and by the presence of large molecular compounds (promoting self-emulsification).

The basic mass of Sakhalin Shelf oil has following characteristics: specific gravity - 0.85 g/sm^3 (light); paraffin content - 0.15 to 4% (low-and-mean-paraffin); sulfur content - 0.09 to 0.4% (low-sulfur); gas content Ð 100 to 150 m^3/t (completely saturated; free gas has a methane composition; the amount of condensed gas is 30 to 150 g/m^3); the amount of oil-asphaltic compounds - 1.5 to 6% (low); contents and ratios of metals (V, Ni, Fe, Mo) vary [2]. As a whole, three groups of oil on the Sakhalin oil field with different ratios of metals can be differentiated (Table 5).

The distinctive properties of oil from the Sakhalin Island Shelf are important from the environmental viewpoint: light oil fractions dissolve better in water [53] and are quickly assimilated by microorganisms; oil with a low sulfur content should have a comparatively less aggressive influence on pipeline material than oil with a high sulfur content.

Oil Transformation in a Marine Environment

Knowledge about the processes of oil decomposition in a marine environment serves as a scientific base on which we can construct a strategy for dealing with oil pollution of the seas and oceans. This knowledge determines the efficiency of chemical and microbiological measures to counteract oil spills. Oil from different origins differs in structure, and these differences increase when oil contacts water and air: the oil's structure begins to vary owing to the loss of part of its hydrocarbons which have minimum molecular mass, density and viscosity, as well as maximum volatility and solubility in the water. At the same time, the properties of oil remaining in a water environment vary in the opposite direction [53].

The complex transformations of oil and its products begin immediately after contact with a marine environment. The course, duration, and the results of the oil's transformation depend on the properties and structure of the oil and on the particular situation and parameters of the environment. The main features of the oil's transformation are: the dynamic (especially in the initial stages) and close interactions of physical, chemical and biological processes in the dispersion of all the oil's components down to their complete disappearance in the initial substrate.

Thus, it is possible to group the following major processes in the transformation of oil when it enters a marine environment [1, 40, 42, 52-66]:

Transport

Oil spilled on the sea surface is initially influenced by the action of gravitational forces and then is controlled by its viscosity and forces of surface tension. A one ton oil spill distributed in a 50 m radius has a thickness of up to 10 mm; the formation of a thinner film (less than 1 mm) covers an area up to 12 square kilometers [64]. As the crude oil spreads, it quickly loses its volatile and water-dissolved components, and the remaining viscous fractions retard the spilling process. The oil film drifts predominantly in the wind's direction with a speed equal to 3 to 4% of the wind's speed, frequently exceeding the rate of water motion [62]. In the course of time, the oil film on the surface becomes thinner and as it approaches critical thickness, (about 0.1 mm), it begins to breakdown into fragments, which are transported over extensive areas. In strong winds, the residues of the oil film are quickly dispersed in a layer of active mixing. Thus, the essential components of the oil turn into emulsified forms and are transported significant distances by currents.

Evaporation

This process is especially important for less dissolved saturated hydrocarbons. During contact with the air, the volatilization of hydrocarbons occurs from the water surface into the atmosphere [53]. During the first several days after an oil spill, a significant amount transforms into a gaseous phase. This amount can make up to 75, 40 and 5 % respectively for easy, mean and heavy oils [66]. The evaporation of low molecular alkanes, cycloalkanes and benzene are the quickest (from minutes up to hours). Polycyclic aromatic hydrocarbons (PAH) (anthracene and pyran types) do not transform into a gaseous phase; they remain in a water environment and are exposed to complex transformations as a result of oxidation, biodegradation and photochemical processes which usually result in the formation of more polar and dissolved compounds. A combination of meteorological and hydrological effects (the power and direction of the wind, waves and currents) determines the specific characteristics of the distribution and the subsequent state of oil in a marine environment.

Solubility

The solubility of oil hydrocarbons depends on their molecular structure and mass. Aromatic hydrocarbons are mostly dissolved, actively passing into a water environment and behaving like truly dissolved substances [53]. Naphthene hydrocarbons seldom dissolve in water. As a rule, when a hydrocarbon's mass increases, its solubility in water is reduced. After oil enters a water environment, the relative enrichment of the dissolved fraction by the most dissolved low molecular aromatic and aliphatic hydrocarbons with their subsequent and rather fast volatilization and increasing of the contribution of less volatile (less dissolved) fractions of aromatic hydrocarbons take place. About 1 to 3% (sometimes up to 15%) of crude oil can pass into a dissolved state. First of all, it concerns the low molecular hydrocarbons of aliphatic order and aromatic structure, as well as polar compounds appearing as a result of oxidizing transformations of some initial petroleum fractions in the marine environment. The transition process into a dissolved state is spread over time and depends on the hydrodynamic and physiochemical conditions of the surface waters. The concentration of dissolved fractions under the oil film in the sea is made up of 0.1 up to 0.3 to 0.4 mg/l [61]. An excess of these concentrations is usually accompanied by the formation of decomposable oil-water emulsions.

Many parameters affect the formation of water-dissolved oil product fractions. The most important among them are: the oil type; the degree and duration of oil mixing with water; the ratio of mixed volumes of oil and water; and the sedimentation time required for the achievement of stable hydrocarbon distributions between water and petroleum phases.

Emulsification and dispersion

Emulsified oil is often the dominant form of chronic oil pollution. This fact is stipulated by the extended action of hydrodynamic factors (wind and others), by receipt of the oil into a marine environment in the form of emulsions, and by the presence of high molecular compounds in the oil pollution's structure (promoting self-emulsification). The formation of oil emulsions in a marine environment depends on the oil's structure and the water's turbulence. The most stable emulsions ("water oil" types) contain between 30 to 80% water. They are usually formed after strong storms in zones of heavy oil spills with an increase in nonvolatile fractions (for example, naphthenes) and can exist in a marine environment for more than 100 days as a peculiar "emulsion" of brown and other tones. The stability of emulsions increases with temperature decreases. "Oil in water"-type emulsions are unstable because of the action of inter-surface tension forces which quickly reduce the oil's dispersion. This process can be slowed down with emulsifiers - surfactant substances with strong water-receptive properties. These substances are used for eliminating the consequences of petroleum pollution. Thus, stabilization of the petroleum emulsion, its dispersion in the formation of microscopic drops and the acceleration of oil decomposition in the water column takes place.

Hydrometeorological conditions are a determining influence on the fate of different oil products at all stages in their distribution in a marine environment. The role of hydrological and meteorological conditions is especially important in the first hours after oil enters a marine environment, when the oil still has low viscous volatility and dissolved fractions. Only in this period is the effective dispersion of oil products possible; small dispersed fractions will not be formed later [53].

Aggregation

Oil aggregates may be frequently found in a marine environment in the form of resinous and mazut lumps and balls (petroleum lumps, tar balls, pelagic tar). They are formed by about 5 to 10% of spilled crude oil and up to 20 to 50% of settled oil and oil products in the ballast and flush waters of tanker holds. The chemical structure of aggregates is rather changeable but its basis is usually made of asphaltic (up to 50%) and high molecular compounds of heavy oil fractions.

Chemical oxidation and destruction

The chemical oxidation of oil in a water environment begins only a day after its entering into the sea. The chemical oxidation of oil is often accompanied by its photochemical decomposition under the impact of an ultraviolet part of solar spectrum. This process is catalyzed by vanadium and is inhibited by sulfur. The final products of oil oxidation (hydroperoxides, phenols, carboxyl acids, ketones, aldehydes and others) usually possess increased solubility in water and increased toxicity.

Microbiological decomposition

Microbiological decay defines the final fate of oil products in a marine environment. There are about 100 species of bacteria and fungus capable of using oil products for their growth. Their number does not exceed 0.1 to 1% of the number of heterotrophic bacterial communities in clean water areas and this figure increases up to 1 to 10% in polluted water [54]. The mechanisms of oil hydrocarbon uptake by microorganisms are the subjects of special laboratory studies [40, 42, 63].

The ability of hydrocarbons to biodegrade depends on the structure of their molecules. Compounds of the paraffin order (alkanes) have this ability to a greater degree in comparison to aromatic and naphthene substances. The rate of microbiological destruction of hydrocarbons usually decreases as the complexity of their molecular structure increases. For example, the biodegradation rate is tens or hundreds of times lower for anthracene and benzo(a)pyrene than for benzene [59, 65]. The biodegradation rate of oil depends on the degree of oil dispersion, on the water's temperature, on the content of biogenic substances and oxygen, as well as on the species' structure and the number of the oil-oxidizing microflora [55, 60].

Oil-based drill solutions impregnated by drill slimes are rather stable in a marine environment. Experiments simulating natural conditions have shown that the biodegradation of oil-based drill waste after 180 days did not exceed 5%, whereas other drill solutions (prepared on the basis of fatty acid esters) were nearly completely degraded (99%) due to microbiological processes and physical-chemical decomposition [57].

Sedimentation

Part of the oil (up to 10 to 30%) is sorbed in suspended matter and settles on the bottom of the seabed. Sedimentation occurs more in narrow coastal zones and in shallow water where the amount of suspended matter is significant and water mixing occurs more frequently. At a greater distance from the coast, sedimentation occurs extremely slowly, except for heavy oils. Suspended oil and its components are subjected to intensive chemical and biological decomposition. On the sea-bottom, the degree of oil decay is sharply reduced since the oxidizing processes slow down due to anaerobic conditions. The fractions of heavy oil accumulated in sediments may be stored there for months and years.

The ratio of dissolved and suspended forms of oil and its components in a marine environment varies in an extremely wide range depending on the particular combination of environmental factors, the structure, properties and the oil's origins. For example, in the Baltic Sea, this ratio varied in the range of 0.2 to 2.1 [52]. A study of oil sedimentation in the Caspian Sea showed that a significant amount of marine salt (possibly in the form of concentrated brine) was found adhering to suspended oil particles. In two samples, 0.3 and 0.1 mg of salt were found respectively in 4.4 and 2.1 mg of oil hydrocarbons [53].

The general conclusion from all the studied processes is that oil quickly loses its initial properties. It is divided into groups of hydrocarbons and fractions of different forms whose composition and chemical structure are considerably transformed. The content decreases owing to the dispersion and decay of the initial and intermediate compounds and the formation of carbon dioxide gas and water. The purification of a water environment polluted by hydrocarbons takes place once the indicated processes are completed.

Oil spill behavior in marine ice conditions

The oil transformation process in ice-covered water areas is slower due to the following factors: an increase of the viscosity of crude oil at low temperatures; restrictions in the oil's distribution owing its adsorption on the ice surface; accumulation in the porous stratum and interstices of the ice cover; and a slow down of the oil's decay by bacterial and photochemical processes in conditions of lower temperatures and restricted oxygen input [1].

During the spring-summer period, the migration of oil into ice capillaries varies from 1 to 49 sm/day. The mean rate of vertical movement of oil into ice is equal to 8 sm/day. Strong winds and currents break up the ice cover and allow the ice to drift. In the Bering Sea, for example, the typical rate of ice drift is 7.4 km/day, and it may increase up to 33-44 km/day during storms [67].

Ecological Requirements and Standards for Waste Disposal

Requirements and standards on discharges from marine drill devices, accepted in many countries and in the frameworks of international agreements, determine the maximum permissible concentrations of certain polluting substances in the total volume of waste. We present one example of these standards (accepted in the USA and Canada for 1987) where norms and limits on pollution during the investigation and exploitation of marine oil and gas deposits are shown [11]:

1. **drill output** - 1100 tons per well during exploratory drilling; stricter requirements during operational drilling;
2. **drill solutions** - 900 tons per well during exploratory drilling; 25% less for the drilling of commercial wells;
3. **cooling, drainage and ballast waters** - should be water- and-oil separated;
4. **layer waters** - should be water-and-oil separated with mean concentrations of oil hydrocarbons at 48 mg/l and a maximum concentration per

day of 72 mg/l;

5. **releases from corrosion protection systems** - releases of small amounts of some metals (aluminum, copper, mercury, indium, tin, zinc) are allowed;
6. **domestic disposals** - should be treated (primary stage of purification).

Methodologies for Controlling the Consequences of Oil and Gas Extraction from a Marine Shelf

There are at least three different approaches to the controlling of the consequences of oil pollution in marine environments. One applies probability methods, one conducts experimental studies, and one performs numerical calculations by using mathematical models.

Probability methods for quantitative assessments of ecological risk

In the last 10-15 years, probability methods for quantitative assessments of ecological risk have been used for controlling the consequences of oil and gas extraction from a marine shelf. This approach is especially used for maintaining ecological safety in conditions of extreme risk. Using similar methodologies, ecological safety problems in risky or extreme situations (for example, emergency oil disposals from wells, breaks in pipelines and other similar accidents) are studied. At the same time, several approaches are used in the application of this methodology for a risk assessment of the consequences of environmental problems in regions where oil and gas deposit development are occurring [68].

In any case, at the first stage, this methodology analyses the opportunities for risk arising. It examines the dangers at different stages of the extraction and transportation processes (disposal of drill wastes, accidents, etc.), and assesses the possible consequences (the degree, character and scale of pollution, biological impacts etc.) and the frequency of the effects (the recurrence of accidents, the dynamics of ecological pollution, etc.).

Experimental studies on the influence of oil pollution on biota

One direction in studies on the influence of oil pollution on aquatic life is connected with the application of experimental system models [69-72]. Some experimental results may be useful for practical purposes in the framework of the Sakhalin Projects:

- Annual experimental studies of the transformations of oil hydrocarbons (mainly paraffins with large amounts of long chain n-alkanes in the C_{20}-C_{35} range) in sediments of a mangrove estuary showed that at first, the decrease in their concentration was determined by physical processes, and then, by biodegradation. Nitrogen deficiency was the main critical factor in limiting the biodegradation rate [73].

- It was determined that at constant low temperatures, the processes of evaporation and weathering were most important in the transformation and spatial distribution of oil products [74].
- Experiments in the Kara Sea showed that only 1% of paraffin hydrocarbon fractions were mineralized per day by microorganisms. The oil-oxidizing activity of microorganisms was developed for about a month after an oil spill in the northern regions. In Arctic waters, the contribution of microorganisms in the self-cleaning of marine waters from oil pollution was about 5% [67].
- In experiments with oil spilled on ice, oil degradation was practically absent because after nine months only a 5% loss in oil mass was registered [67].
- Experiments were conducted to measure the visibility of oil slicks [75], oil photo-oxidation [76], oil biodegradation [77], the stability of oil emulsions [78] and oil dispersants [79], and the ability of marine microorganisms to produce bio-dispersants to degrade crude oil [80].

Numerical modeling and forecasting

Another direction of studies is connected to numerical modeling and forecasting hydrocarbon distributions in a marine environment. These studies combine the scientific disciplines of applied oceanography and marine ecology.

Many models describing various scenarios for the movement and dispersion of oil pollution have been developed in many countries. They consider the possible consequences of oil spills and are sometimes helpful in preventing and cleaning up oil pollution [9, 23, 81-85]. Models that take into account the mechanisms of oil hydrocarbon transformations in an aquatic environment have also been developed [86].

Experience in the application of these models shows that their efficiency in the prevention and clean-up of oil spills is finely defined by the availability of the necessary data. This data should include the oil's characteristics (oil type, its properties, volume and rate of spillage), and environmental parameters (the speed and direction of wind and currents, depth, temperature, etc.). Unfortunately, the required information is seldom available and in the necessary quantities [84, 85]. The creation of data banks for regions where emergencies are especially probable will doubtless increase the model's reliability and effect on forecasting assessments.

See Figure 5 for an example of this model which looks at the Sea of Okhotsk [87]. This model will allow us to comprehensively evaluate the state of the Okhotsk Sea ecosystem and to add available information about the variability of major parameters: biogenic compound concentrations, biomasses of micro-organism communities and the parameters of their productivity in different marine basins.

Evaluations and forecasts made within the framework of the Shtokman condensed gas deposit in the Barents Sea [31] are especially interesting. One study considers the possibility of a mixture of gas, condensed gas and layer water in volumes of 8 to 38 million m^3/day, and a large-scale spill of condensed gas of 10,000 to 100,000 cubic meters from an opened well for a month. The calculations of the drift and dispersion of oil after such spills during various weather and ocean conditions in the Barents Sea showed a possibility of hydrocarbons moving tens or hundreds of kilometers from their place of origin with a real risk of destroying (or damaging) marine organisms in an area up to 1400 square kilometers. This means that if a similar accident were to occur in the Okhotsk Sea, practically the entire area (the sea is about 1590 square kilometers) may become polluted and that a real risk of destruction will exist for a greater part of its biological marine resources. It is also possible to assume that the system of water currents in the coastal zone of Sakhalin Island [88] will transfer polluting components in a southern or southeastern direction. Thus, there is a great probability that pollution will reach the coast of Japan.

Conclusion

International experience shows that the development of oil and gas fields in the seas and oceans inevitably results in complex ecological problems connected with pollution of the marine environment and the destruction of biological resources.

Obviously, the extension of large-scale oil and gas extraction from marine deposits (especially in the Arctic and the Far East Region) is not desirable for the preservation of biological marine resources.

Regular hydrochemical and biological observations should be started to control the state of the marine environment in areas of oil and gas extraction on the Sakhalin Island Shelf.

Numerical models should be developed to simulate the different types of disasters caused by oil and gas extraction in the environment near Sakhalin Island, in particular, to predict the distribution of spilled oil in the short and long term.

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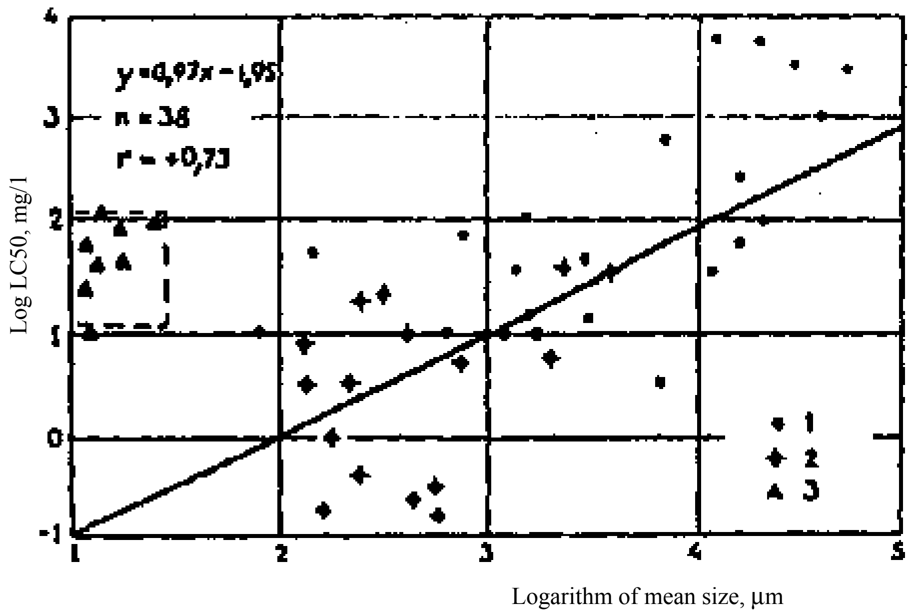


Fig.1 Correlation between the oil product concentration (LC50) for marine organisms with their size characteristics [1]:

1 - adult species; 2 - early stages of ontogenesis; 3 - values of effective concentrations (EC50) for unicellular algae; n - numbers of data; r - correlation coefficient; (dash line indicates data do not taken into account in calculations).

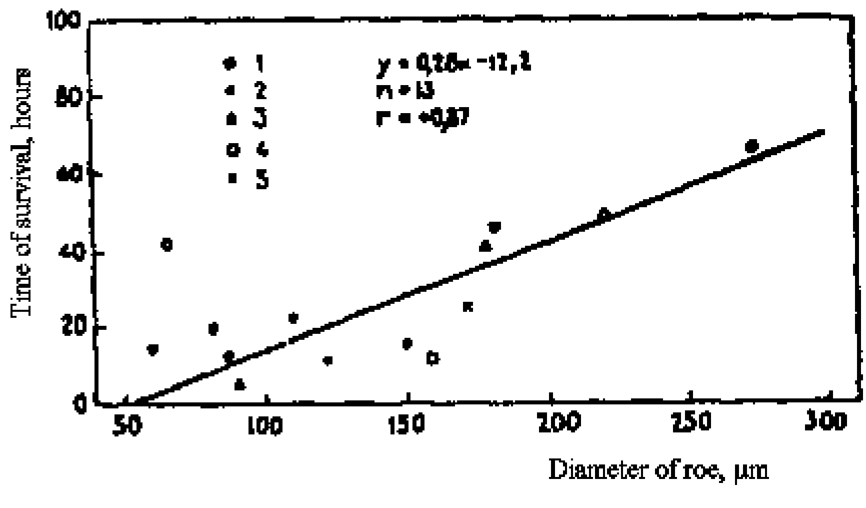


Fig.2 Correlation between the survival time of growing roe of marine invertabrates with the roe size at the incubation into 0.5% solution of diesel fuel and sea water [1]: *1 - Molluska; 2 - Echenodermata; 3 - Annelida; 4 - Urochordata; 5 - Arthropoda (Balanus cariosus).*

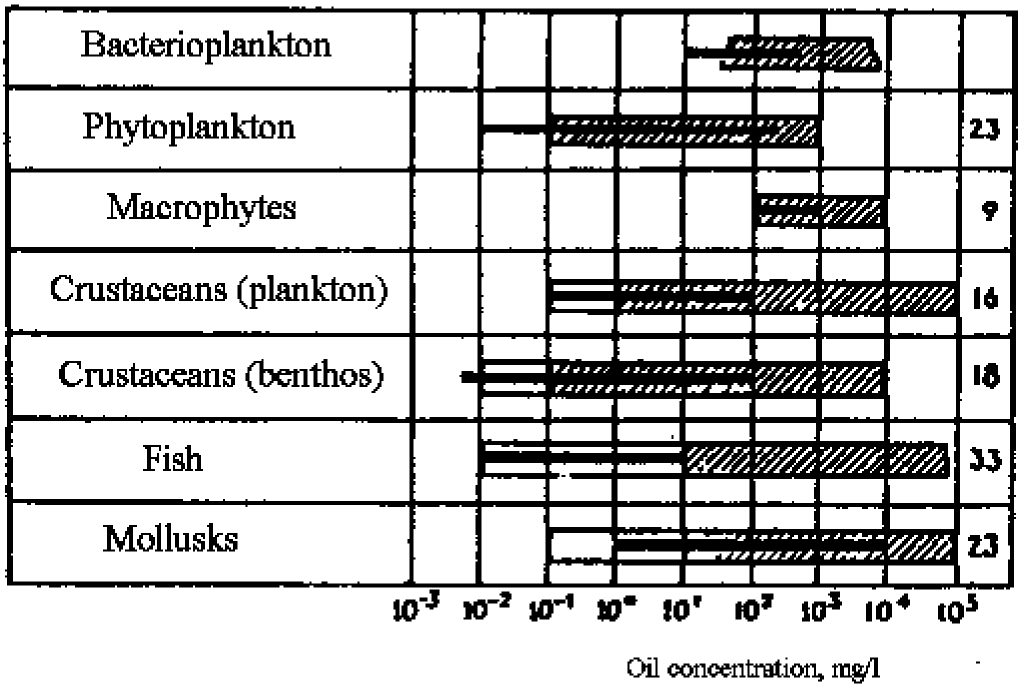


Fig.3 Range of toxic (rectangles) and treshold (fat lines) concentrations of dissolved oil fractions for basic marine organism groups (unshaded part - areas of toxic concentrations for early stages of ontogenesis; numbers in right side - amount of studied species). Toxic concentration indicate ranges of the content in environment at which measured indexes have reliably decreased more than on 50% from the control in experiments continued 2-4 days. Treshold concentrations indicate the minimum content in environment at which measured indexes have decreased on 50% in experiments comparable in the time with ontogenesis of studied organism [1].

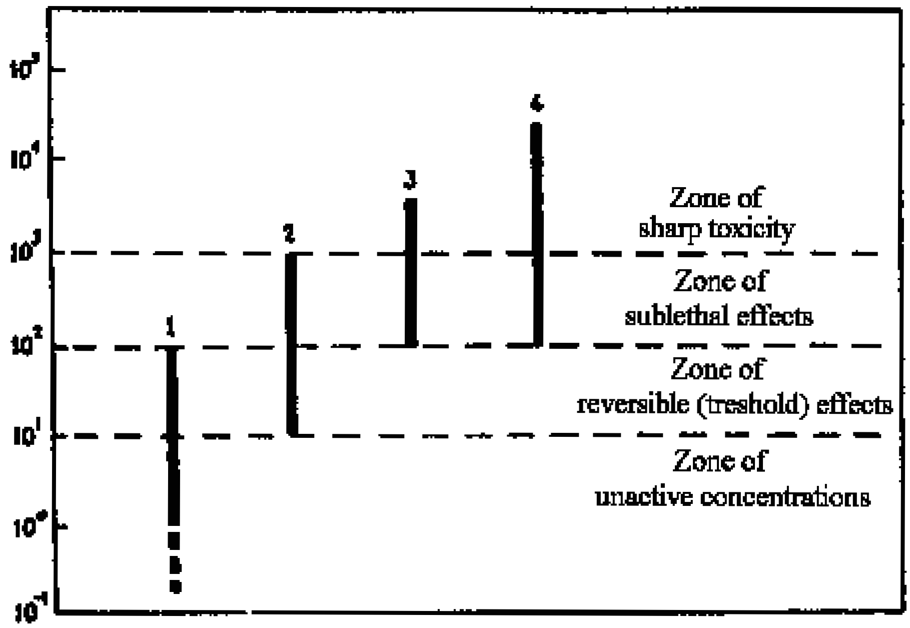
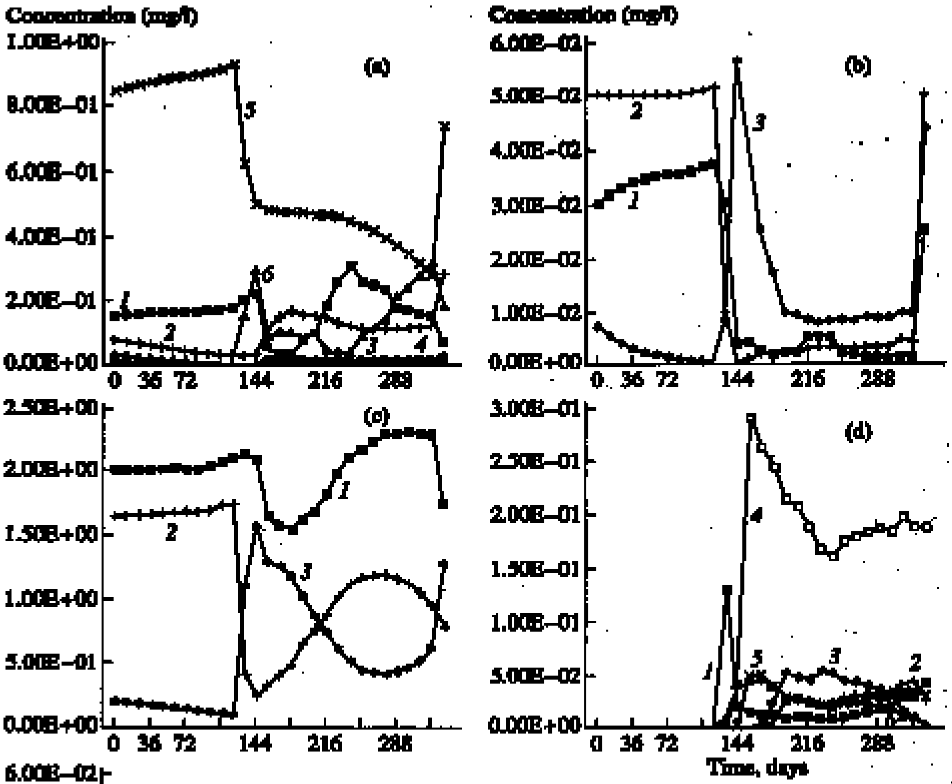


Fig. 4 Approximate levels of biological action and ranges of specific oil hydrocarbon content in sediments [1]:
1 - pelagic zone of seas and oceans; 2 - coastal zones; 3- bays, estuaries, inlets, ports and other, 4 - areas of strong pollution at oil spills, disposals and etc.



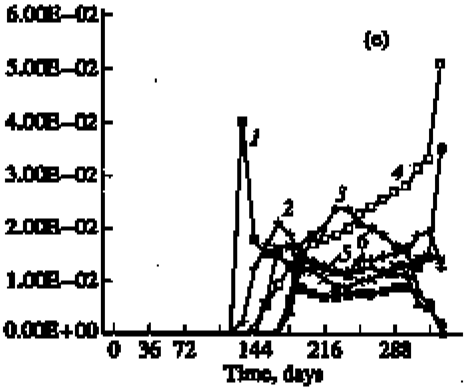


FIg. 5 Calculated variations in concentrations of organogenic element compounds for Area 1 of the Okhotsk sea: (a) forms of N (1 - DON; 2 - UP; 3 - NH4; 4- NO2; 5 - NO3; 6 - ND); (b) forms of P (1 - DOP; 2 - DIP; 3 - PD); (c) - Corg (1) and forms of Si (2 - SiO4; 3 - SID); (d) biomasses of organisms in terms of N (1 - F1N; 2 - F2N; 3 - F3N; 4 - B1N; 5 - Z1N; 6 - Z2N); (e) biomasses of organisms in terms of P (1 - F1P; 2 - F2P; 3 - F3P; 4 - B1P; 5 - Z1P; 6 - Z2P).

Table 1.
Potential waste from marine devices for drilling and recovery of oil and gas [8].

Operation	Disposals
Exploring and industrial drilling	water- and oil-based drill solutions; drill output (slime); cement remains
Packing of well-drillings	Tamponage solutions and reagents
Repair of well-drillings	repair liquids, corrosion inhibitors and precipitate
Technological operations in the extraction and treatment of hydrocarbons Accidents	Compounds for the separation of mixtures containing oil, gas, and water; passing (layer) water; water and reagents pumped to well-drillings; cooling water; drainage water; domestic wastes and discharges; atmospheric discharges
	Spills of oil and reagent solutions

Table 2. Approximate amounts of waste produced in the exploration and recovery of oil and gas in the sea [9].

Type of waste	Approximate amount, tons
In areas of exploring drill per one well:	
used drill solution (periodic disposal)	15-30
used drill solution (total disposal)	150-400
drill slime (dry mass)	200-1000
oil in drill slime	300-1200*
In areas of oil recovery for well-drillings system :	
used drill solution	45000**
drill slime	50000**
layer and productive water	1500 tons/day ***

Notes: * Actual amounts may be higher [10];
** Assessment is done for 50 wells drilled from one platform in the period from 4 up to 20 years [11];
*** For one platform [12].

Table 3. The influence of development on ecological factors during different stages of development of marine oil and gas deposits [1].

Stage	Aspect of activity	Type and character of the influence
Geological and geophysical exploration	seismic prospecting exploring drilling conservation and liquidation of well-drillings	disturbances for fishing and for other users; influence on biota and fish resources; perturbation on the sea bottom; alienation of water areas; technological disposals; discharges to atmosphere; accidental conditions disturbances for fishing and for other users
Preparing of well-drillings	testing of well-drillings assembling the drill platform; construction of pipe-lines, shore buildings and etc.	(see exploring drilling) physical perturbations; disposals of liquid and solid wastes; disturbances for fishing (platforms, pipe-lines) and for other users
Exploitation	drilling, technological transport and other working activities	technological disposals at the drilling and recovery; accidental oil spills and disposals; alienation of water areas; disturbances for fishing and for other users
Completion and	disassembly of platforms and pipe-lines, conservation of well-drillings and other operations	disposals; alienation of water areas; disturbances for fishing and for other users

Table 4. Total characteristics of the influence on the water ecosystems and their biorecources at different activities of the oil- and gas deposit development [1].

Character of influence and consequences	Seismic prospecting	Construction of platform and other	Drilling activity	Transport by: pipe-lines	Transport by: tankers	Accidents
Physical effects on:						
Pelagic spieces	+	+	-	-	+	+
Bottom biocenosis	+	+	+	+	-	+
Bottom biotope	+	+	+	+	-	+
Disposals to atmosphere	-	-	+	+	-	+
Alienation of water areas	-	+	+	-	-	+
Disturbances for fishing	+	+	+	+	-	+
Perturbation in fish migration	+	+	-	+	-	+
Chemical pollution	-	-	+	-	+	+
Increase of water turbidity	+	+	+	-	-	+
Deterioration of commercial quality of industrial species	-	-	+	-	+	+

Notes: signs plus (+) and minus (-) mean respectively the presence and absence of the specific influences at different activities.

Table 5. Types of oil in Sakhalin Shelf area in respect of microelement content [2].

Group	Type of concentration ratio	V / Fe	Oil Field
I	V > Fe> Ni > Mo	2.0	Odoptu
	V > Fe > Mo > Ni	2.9	Odoptu
	V > Fe> Ni > Mo	2.3	Pil'tun-Astokhskoe
	V > Mo > Fe > Ni	7.5	Odoptu
	V > Ni > Fe > Mo	8.0	Odoptu
	V > Mo > Fe > Ni	1.4	Pil'tun-Astokhskoe
	V > Ni > Fe > Mo	4.0	Arkutun-Daginskoe
II	Fe > V > Ni > Mo	0.6	Pil'tun-Astokhskoe
	Fe > V > Ni > Mo	0.7	Pil'tun-Astokhskoe
	Fe > V > Mo > Ni	0.4	Pil'tun-Astokhskoe
	Fe > V > Ni > Mo	0.4	Pil'tun-Astokhskoe
	Fe > V > Ni > Mo	1.5	Pil'tun-Astokhskoe
	Fe > V > Mo > Ni	0.7	Pil'tun-Astokhskoe
	Fe > Ni > V > Mo	0.4	Daginskij area
	Fe > Ni > V > Mo	0.5	Daginskij area
	Fe > V > Ni > Mo	0.9	Daginskij area
	Fe > V > Ni > Mo	0.8	Daginskij area
III	Ni > Fe > V > Mo	0.8	Daginskij area
	Ni > Fe > V > Mo	0.8	Daginskij area
	Ni > V > Fe > Mo	3	Chaivo
	V > Fe > Mo > Ni	1.5	XIV layer in Chaivo