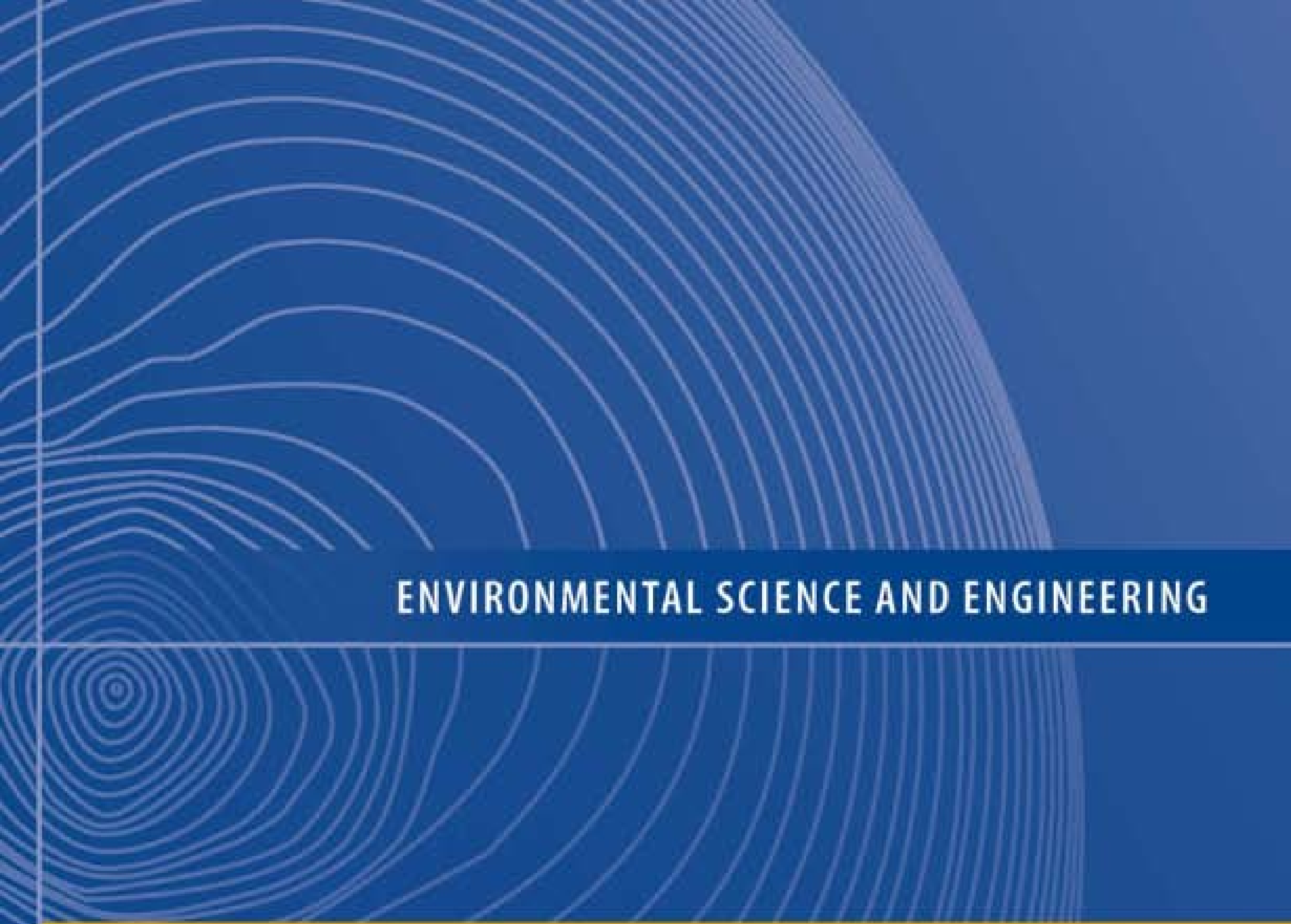

ENVIRONMENTAL SCIENCE AND ENGINEERING

Dmitry Ya Fashchuk

Marine Ecological Geography

Theory and Experience

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Preface

As a totality of scientific disciplines studying physical, chemical, biological, and geological processes in the ocean, oceanology moves toward geography of the ocean… running up to generalization of regularities of processes in natural complexes. Furthermore, its aim is to develop physico-mathematical model of all factors...

Acad. K. K. Markov, 1970

In Declaration "Agenda 21" adopted by the UN 1992 Conference on Environment and Development (Rio de Janeiro), practically for the first time in the history of economic management on our planet, the heads of states and governments, World's leading industrialists and scientists avowed, at last, the necessity of transition from random exploitation of natural resources to sustainable development for conservation of biosphere and, therefore, ourselves.

As it is known, the term "sustainable development" was formulated first in 1987 in the report of World Commission on Environment and Development (Brundtland Commission). It implies the establishment of contemporary economic management in such a way that future human generations will have a "field of operations" to satisfy their needs. At the first glance, the scheme of realization of the above statement seemed very simple:

- rates of renewable resource consumption nowadays should not exceed rates of their natural recovery;
- rates of development and introduction of technologies for artificial production of non-renewable raw material sources should be higher than rates of their depletion;
- volumes of dumping and burial of industrial wastes should not exceed the waste assimilative capacity of the environment.

However, the results of the first 10 years of the world community development under the banner of "sustainable development" strategy, summarized at the World Summit of Heads of the States (Johannesburg, 2002), showed that implementation of its main statements was far from "clockwork" and run against considerable difficulties.

Several interrelated circumstances directly relevant, in the author's opinion, to problems of efficiency of realization of environmental measures and rational resource exploitation on marine aquatories, component of the Agenda 21 concept of sustainable development, served as cause and motivation for preparation of the present monograph.

1. Among the causes resulting in problems at implementation of new concept, the paradigms of human thinking and blatant ecological ignorance at all levels of world social organism, from government officials to heads of industrial and agricultural enterprises, from majority of leading scientists to schoolteachers and readers, not to speak of ordinary workers and peasants, are not at the bottom.

Over the past "triumphant" century of scientific and technological progress for the years of numerous socialistic 5-year plans and capitalistic booms, the human community in its restless desire of better life, earning a lot of money, has lost somehow unnoticeably the instinct of self-preservation, disengaged from the major object of economic activity and source of its prosperity—Mother Nature. As a result, in the present twentyfirst century its crass "king" (even with Ph.D. or portfolio), instead of commandment "do not harm", still follows the light-minded thesis "somewhere we lose, somewhere we gain" or "profit at any price", continuing to camouflage the real principle "after me the deluge". The sad experience of such substitution has matched to the full extent the well-known saying "the road to hell is paved with good intentions" (Fashchuk 2005). The developers of the theory of sustainable development supposing the necessity to realize the principles of social fairness, economic development, conservation of the high-quality environment for achievement of this objective, did not take into account a huge inertia of human thinking which affected the time frames and efficiency of problem solving.

The appropriateness of the above suggestion is confirmed by the history of concept of biosphere as planetary ecosystem (Abakumov 1991). The speculations regarding dependence of life on the Earth on environmental conditions appeared in scientific community beginning from the second half of the sixteenth century. By that time, together with the flow of wealth sprung into the Spanish treasury from the New World discovered by Columbus (1492), the capitals and big cities of the leading European countries filled with a vast number of exotic plants brought by conquistadors to their sovereigns and friends as "souvenirs from America". As a result, the artificial corners of nature, botanic gardens, started to appear and develop actively (1545 Padua, 1547 Pisa, 1567 Bologna, 1577 Leiden, 1593 Heidelberg, 1623 Moscow, etc.). But it emerged that at the European conditions plants brought from the four corners of the earth behaved differently and, thereupon, required individual care. Naturally, the scientific idea responded instantly to this phenomenon and started to work actively for its description, theoretical explanation, and practical use.

Only 300 (!) years after this "discovery", in 1866, German biologist Ernst Haeckel (1834–1919) suggested the term "ecology", then, in 1875 Austrian geologist Eduard Suess (1831–1914) formulated for the first time the notion "biosphere", and, finally, in 1877 German zoologist and microbiologist Karl

Mobius (1825–1908) suggested the definition “biocenosis”. Thereafter, it took more than 50 years for these categories to become common in the scientific practice and to get further development—only in 1935 the theory of ecosystems by English phytocenologist Tansley was published, and his term “ecosystem” came into natural science. In 1940 Russian geobotanist Vladimir Sukachev (1908–1967) developed the concept of biogeocenosis which was very close to ecosystem.

Thus, **it took more than three centuries** even for scientific luminaries in order to the concept of ecosystem approach slipped from formal knowledge to deep knowledge. It is easy to calculate that after this principle “naturalized” in scientific minds (1935–1940) only half a century (!) passed away until the UN 1992 Conference in Rio de Janeiro, and even much less time—from adoption of the Agenda 21 to nowadays. It remains only to take off hat to optimism of authors of sustainable development concept, believed naively that for this historic blink it was possible to “change the brains” of ministers, businessmen, farmers, and a majority of other ordinary people, decisions and actions of which affected the success of mankind’s “struggle for survival”.

After such a simple analysis many facts registered by both national and foreign specialists in the field of natural resource exploitation and environment protection become clear. For example, only in the 1970s–1990s dozens of decisions and resolutions on ecology and marine environment protection have been published in Russia and abroad. All of them appealed “to concentrate”, “to enhance”, “to consolidate” Aibulatov (2005). The sentences “complex system approach”, “ecological monitoring” were constantly presented in the national and international programs on investigations of any given sea or region of the world’s ocean. Their result is well-known for us…

Following the logic of the above analysis, the appeals, slogans, and directives were formal and untimely. They were addressed to the emptiness and could not be realized because there was no deep insight in consciousness of potential executives, regarding what it meant and why it was necessary. That is why even today, despite the long history of investigations, the solving of many marine ecological tasks continues for a long period, often remaining only at the hypothesis’ level.

2. In the late twentieth century—early twenty-first century the monitoring system, in which the researchers believed, made a lodgement in practice of marine resource use. Its realization at conduct of any operations (especially associated with mineral prospecting and mining, development of aquaculture, etc.) really allowed to collect the huge banks of data characterizing environmental conditions and their variations in corresponding marine areas. Nevertheless, the results of monitoring are rarely analyzed in complex for functional practical and predicting conclusions.

This situation is determined not only by a huge volume of observations carried out during the monitoring period and, therefore, an objective lack of time for researchers to analyze and predict the results. Its reason is associated with a lack of methodological principles for operative analysis of information obtained and appropriate skills of executives.

Now, in most cases the qualified engineers and observers familiar with methods of formal mathematical and computer analysis, methodologies of physical, chemical, biological and other types of analytical determinations but, unfortunately, indisposed to creative abstract thinking and system analysis, are dominated in solution of these problems. Naturally, under such an approach the key in their work is to make methodically correct observations, to describe their results formally, to render a report in time, to defend an estimate of expenditures, and to draw up funding requirements for the next year but not, for example, to clear up the causes of fish kill or anomalous state of marine environment.

As a result, the invaluable collected data remain useless in archives and funds of oil producing and other companies. They allow to answer the questions on what kind and when the sea can be, what and how much the sea contains, who and in what number inhabit the sea, and, at the best case, to assess the temporal and spatial tendencies in marine ecosystem components. But, unfortunately, these data do not allow to learn, why the sea is such, by what reason the changes occur, what will happen if external forcing changes. As a result, the industrials fulfilled formally the demands of another resolution in the field of rationalization of natural resource use, continue to kill the nature blindly on the way to "future prosperity".

It is impossible to understand and predict the life in marine basin at command. This calls for not only a trained observer but scientific analyst, who is able to assess and use the achievements in different fields of marine science in order to solve the system of "integral equations" such as the current marine ecological problems, to analyze the information, forecasting estimates, and functional practical conclusions. He must possess an universal interdisciplinary style of thinking and scientific intuition but training of ecologists able to think comprehensively and creatively, to doubt, and to feel the nature, occurs in Russia very slowly, not to speak of other countries. None of directives and resolutions can fill this deficit, which means that it is impossible to improve quality of diagnosis and forecasting of marine ecological situations, to realize operatively the principles of concept of sustainable development in this field of natural resource exploitation.

3. In the 1990s, after the UN Conference in Rio de Janeiro, the interest in ecological problems has grown considerably. This has become apparent, first of all, in creation and development of the system of ecological education, though since the 1980s Environmental Education has already existed in the world practice. In the United States and some European countries the associations of ecological education have been organized, and the future ecologists have been learned at chairs "Environmental Sciences" or "Environmental Studies" in universities of many countries.

In addition to summarizing the results, the World Summit (Johannesburg 2002) outlined the ways of efficiency enhancement for further implementation of sustainable development concept (Glazovsky 2003). In particular, the implementation of declaration Agenda 21 (1992) required the new type of education, Education for Sustainable Development" (ESD), for sustainable development, for the purpose of sustainable development, for sustainability. Its conceptual basis differs principally from the earlier existed ecological education, first of all, that it does not provide strict “vertical” of educational process. Thus, the objective of ESD is not to decide “Where we are now” but to learn “***Where we should go***”; the intention of ESD is not a concrete product ”Getting of skills“ but the process “***Development of competence***”; result of ESD is not an instruction “How to make money” but the wish “**To participate in further education**” (Mazurov 2003; Kasimov et al. 2004, 2005; Sadovnichy and Kasimov 2006).

Therefore, the ESD system is based on quite different conceptual and methodological principles. The educational program here is not a “Final scheme” but “***Experience, consideration of specific situation***”, the gained knowledge are not “Fixed, but abstract and unified” but “***Changing, but real and multivariate***”. Thus, the new ESD system turns the traditional “Passive education and its result—niche specialism” into “***Active education and its result-broad, flexible, interdisciplinary knowledge***”. With that, “Educational system” becomes ***System of learning***, and “Formal education” transforms into “***Education durante vita***”.

In the Soviet Union, quarter of a century before the UN 1992 Conference the concept of rational use of natural resources, very close to the idea of sustainable development, was developed. In the early 1990s under this concept the new specialty “Environment protection and rational use of natural resources” was created. Ecological education in *traditional* universities included the specialties “Ecology”, “Geoecology”, “Natural resource exploitation”. In technical universities there was the courses “Life safety” and “Environment protection”. Now the first version of National Strategy of ESD was developed for traditional Russian Universities. According to this strategy, the students will gain broad, interdisciplinary systematic knowledge based on complex approach to development of society and economy of environment (Sadovnochy and Kasimov 2006).

Owing to financial support from Moscow Foundation of Schoolbook Industry created by Moscow Mayor Yuri Luzhkov, in 2006–2007 the publishing house OJSC “Moscow Schoolbook” brought out a series of author’s books addressed to future generation of marine ecologists and their schoolteachers under the common title “Under the jolly Roger to mysteries of the ocean” Fashchuk (2006a, b; 2007a, b, c). In five volumes of “Reading Books for future Magellans” the author attempted, in popular form, to attract attention of youth to marine ecological problems, to acquaint them with history of investigations of the world’s ocean and evolution of our planet, to touch the mysteries of the germ of life, to tell about its diversity, to acquaint with environmental factors and natural processes—“conductors” of this life, wealth of mineral resources in the ocean, to present the role of mankind in the ocean’s life, positive and negative consequences of their interaction. Nevertheless, ***until now there are no universal textbooks on the mentioned disciplines for higher education***.

4. Finally, there is one more fact occasioned the preparation of the monograph. At present, as a result of active development of computing techniques and computational mathematics tool, together with field observations in the sea, the mathematical models became a basic component for scientific understanding of ocean’s nature, an important element at solving of specific ecological tasks. Now hundreds of different models are developed throughout the world. They help

researchers to understand the mechanisms of functioning and interaction of marine ecosystems, to forecast possible changes in marine environment, to learn how to take control on its state. Nevertheless, despite the progress in modeling (in terms of the number of developed models), the ocean still takes time to evolve its "secrets" to mathematicians, physicists, chemists, biologists. Today, the reliability of marine ecological forecasts developed on the basis of model analysis leaves, mildly speaking, much to be desired. Some of national models, even awarded state prize during the modeling boom of the 1970s, fell into oblivion long ago because, in practice, they showed themselves to be just an instrument for exercises in calculations having little in common with the real nature (Fashchuk et al. 2005).

The conclusion that any mathematical model is just a tool in researcher's hands, is not original. In other words, the quality of modeled forecast depends on the quality of used information based on understanding of modeling object nature. And yet in ancient times classic of antique philosophy Aristotle knowing better imperfection of many his theories believed that *Attainment of truth is both easy and difficult as it is evident that nobody can either comprehend it fully or overlook it completely, but everyone adds little to our knowledge of nature, and in the aggregate these factors form the majestic picture*. Indeed, because of individual peculiarities of human conscience, his education and many other reasons there are many scientists in the world now which know "everything", for example, about the World Ocean. But really among them nobody knows "everything correctly". The absence of attempts to put together individual knowledge, "all these facts", is a reason that, unfortunately, a long-expected *majestic picture* is "developed" very rarely.

It is a geography which connects man and nature! Searching and true understanding of its laws, cause-effect relationships by physicists, chemists, biologists, mathematicians are inefficient without geographers. The world research experience evidences that today the representatives of many fundamental sciences solving the practical problems of marine ecology (and indeed not only marine ecology) obtain desired result very rarely (Medouz and Randers 2007). The author takes leave to suggest that a reason for this lies in passive, very "timorous" participation of geographers in the process. After all these were geographers who were ordained by fate to breathe life into equations and formulas of ecological models, to provide the "aggregate" of used data. The history of geographic science development confirms reality of this suggestion.

In 1942 Vice President of Academy of Sciences of the USSR academician Fersman (1883–1945) in his paper "Geography and war" noted that geography considered as a descriptive science, has become the leading force at solving of most important problems of world conflict. Explaining the reasons for this, he emphasized that *geography is anything but science about several facts of outside world. Geography is a science about the existing relationships, ratios between phenomena and man laboring in nature*. In this relation, the practical significance of development of geographic and ecological research for mankind seems as important as contribution in due time of Soviet military geographers to the victory over fascism (Abramov 2005).

In the post-war years academician Gerasimov introduced term *constructive geography* into natural science, emphasizing the importance of geography at solving of not only military but practically important economic tasks. *Military geography* was one of its directions. In present changeable world another direction of constructive geography, *ecological geography*, gains particular actuality (at the level of fundamental sciences).

In the 1970s Soviet geographer academician Konstantin Konstantinovich Markov (1905–1980) became one of the originators of theoretical bases of physical geography of the World Ocean. Noting necessity of contingence of differentiated sciences on the basis of unifying geography science, he determined the essence of geographic approach at research on the man–nature interaction. It his opinion, it consists in *learning of aggregative geographic conditions, study of natural phenomena in their unity, interrelation, and causality.*

Among objectives of physical geography, along with study of spatial structure, Markov outlined the research on interrelationship of ocean nature and continents, natural resource exploitation, and *impact of social reproduction on the ocean and ocean on social reproduction*. Herewith, both the planetary geographic regularities of oceanic life and specific physiographic features of this component of biosphere are studied.

In the early 1970s the team of colleagues supported the Markov's idea and consisted of specialists in the field of ocean physics (Lebedev), marine chemistry (Aizatulin 1939–2002), and marine biology (Khailov), proposed a concept of necessity of transition from factographic knowledge to system analysis of physical, chemical, biological and other processes forming environmental conditions and determining the state of marine hydrobionts. In the following, the authors developed the theory of Vernadsky regarding biological structure, role of boundary layers in "accumulation" of marine organisms—"concentrating of life". The approach allowed to consider an object from all sides, to understand its nature using the *optimum* of information. With its use, in 1973 the existence of biologically active centers on ocean bottom was predicted (Aizatulin et al. 1976). These centers, 'oases of life', based on chemosynthesis were found soon by submersibles off the Galapagos Isles in the Pacific Ocean (depth about 3 km).

Unfortunately, the proposed concept was not developed by marine scientists in the late twentieth century. The paradigms of contemporary natural science were stronger, and monographs of the authors *Ocean as a dynamic system* (1974), *Ocean*: *active surfaces and life* (1979), *Ocean: fronts, dispersion, life* (1984) and their digest in English *The Living Ocean* (1989) have remained practically uncalled until now.

By the beginning of the twentyfirst century the economic activity on coastal aquatories has been intensified sharply. Only in 1996–2000 the annual oil production has increased from 10% to 25%, equaled to 0.7–0.9 billion t in absolute values. The world annual gas production in the late twentieth century has reached 2,000 billion m^3, and share of marine developments has exceeded 20%, constituting more than 300 billion m^3. Herewith, the total world oil reserves for 2008 are estimated as 200 billion t, and those for gas, 175 trillion m^3 (Radler 2008). In parallel, there has been an intensification of marine transport operations, laying of oil and gas pipelines, development of fish farms and aquaculture farms for cultivation of mollusks and seaweeds, construction of ports, objects of marine tourism and recreation. The ecological consequences of such an anthropogenic stress on marine ecosystem constitute the object of a new direction of geographic science-**marine ecological geography**.

Object of its study—*spatial and temporal variability in the casual-effect relationships between abiotic and biotic components of marine ecosystem under the changing natural factors and economic activity.*

Objective of study—*causes of change in marine ecosystem state and forecast of ecological consequences of natural and anthropogenic forcing for development of scientific bases of marine resource management and exploitation.*

The methodological principles of this direction of geography have not been formulated yet. Following the logic of proposed definitions, the responsibility for formulation and solution of marine ecological problems, as it was supposed by Markov 30 years ago (Markov 1970), lies, first of all, on geographic oceanologists because it is a science which is the most capacious marine geographic discipline. Incorporating physics, chemistry, biology, geology of the ocean, it studies the corresponding processes in marine environment and has the ability to combine professionals of different specialties for achievement of target goal.

The proposed monograph includes the results of theoretical developments and practical solutions of the author—oceanologist obtained in the process of formulation of principles of marine ecological geography and their realization at Institute of Geography of the Russian Academy of Sciences under:

1. Project of basic research of the Russian Academy of Sciences *Natural processes in the external Earth's envelopes under increasing anthropogenic stress and scientific bases of ecologically safe rational use of natural resources* (2001–2005).
2. Grants of the Russian Foundation for Basic Research: No. 98-05-65031 *Evolution of hydrological systems with zones of hydrosulfuric contamination* (1998–2000); No. 00-05-64166 *State of marine ecosystems with account of the contemporary oil and gas field development on the shelf* (*taken the Black, Caspian, and Okhotsk Seas as an example*) (2000–2002); No. 01-05-84778 *Geographic regularities of anaerobic condition formation in the Earth's hydrosphere* (2001–2003); No. 03-05-64505 *Transformation and cycle of nutrients and organic matter in the White Sea ecosystems: analysis with the use of mathematical modeling* (2003–2005).
3. State contract No. 02.515.11.5037, subject 2007-5-1.5-16-02 *Development of scientific and methodological bases for estimation of the Russian marine ecosystem tolerance to extraction and transportation of hydrocarbons with the purpose to organize the system of complex ecological monitoring under different climatic conditions* (2007–2008).
4. Russian–Ukrainian Grant of the Russian Foundation for Basic Research No. 09-05-90415-Ukr_f_a *Geographic and ecological assessment of consequences of*

hydrocarbon exploration and transportation for environmental conditions and biodiversity of underwater landscapes in the Kerch Strait (2009–2010).

In Chap. 1 of the monograph the methodological principles of systemization and visualization of multidimensional ecological information for its operational dissemination among potential users are stated. Their realization results in the development of geographic-and-ecologic model of marine basin as an information base for diagnosis of the marine ecosystem state, estimation of consequences of economic activity, and modeling of its changes with the use of mathematical tools.

In Chap. 2 the geographic and ecological aspects of mathematical modeling of marine ecosystems, capabilities and features of the most relevant models such as the Russian hydrodynamic model of oil spills "SPILLMOD" and hydroecological model of organogenic compound transformation in the sea, are considered.

In the following six chapters the examples of practical realization of geographic and ecological (as a source of information) and mathematical (as a computing tool) modeling at investigations on specific ecological problems associated with consequences of natural hazards and economic activity both on aquatory itself and within the whole Black Sea basin are given. They include: history of hydrological structure formation and causes of the present dynamics of the H_2S-zone upper boundary (Chap. 3); causes of summer suffocation event development (death of bottom hydrobionts) on the northwestern shelf and their relation to regulation and changes in qualitative composition of the Dnepr and Danube discharge (Chap. 4); consequences of marine gas production in the Karkinitsky Bay and prognosis of time required for its self-purification from oil pollution (Chap. 5); prognosis of possible impact of marine fish farms on environmental conditions off the Russian North Caucasian Coast in the area of Great Sochi (Chap. 6); consequences of economic activity in the Kerch Strait (Chap. 7); consequences of the tanker VOLGONEFT-139 wreckage as a result of the unusual storm (11 November, 2007) in the Kerch Strait (Chap. 8).

In Conclusion the main world problems of the present marine resource exploitation, relevant directions of scientific research and international cooperation associated with the study of role of the World Ocean in changes of environment state on our planet are analyzed. The comparative assessment of structure, goals and objectives of Federal Target Program "The World Ocean" (1998) and the U.S. Project on the World Ocean research "Turn to the sea: future of the United States is in the World Ocean" proposed by former vice-President of the United States Gore (1999) is made. It is concluded that the effectiveness of results of both projects depends in large extent not only on volume of funding but on the scale of engaging of geographic scientific tools to their realization.

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Contents

Chapter 1
Geographic and Ecological Information Model of Marine Basin

In the early 1980s, being in Kiev at the representative technical council debated the problem on expediency and possible consequences of construction of the Dnieper-Bug hydraulic center, I had occasion to explain performers of the work, specialists of the large planning institute, what expected the Black Sea in case of realization of another "project of the century". I diluted with enthusiasm on tens of thousands of dead fish, increasing volumes of fetid municipal sewage runoffs, saprobic water reservoirs, and many other possible consequences of construction of another dam on the Dnieper. Despite all my emotions, there was no tears in the room. The reaction of audience on information was more than calm. The discussion was closed with traditional question: "How much is your nature?". This meant the sum of compensation for doing damage to nature.

Only after a decade it became clear that the reason of my fiasco lay not in a lack of sound arguments but in that the mentioned facts did not represent a consistent sequence of the cause-effect relationships which would allow to incorporate the audience and "object", to show their place in the structure of relationships between civilization and nature. In that time it was impossible to develop such a logical scheme because of the wealth and diversity of information under a lack of methods for its systematization, matching, visualization, and multiplicity of interdepartmental relations and stereotypes of professional thinking.

The following analysis of numerous attempts to estimate the state of marine aquatories showed that the diagnosis and, further, the forecast of marine aquatory state at the end of the twentieth century were far from perfection. In particular, although more than a dozen of scientific research institutes and other organizations studied the Black Sea were located and functioned successfully on its coast and watershed at the end of the last century, it took 5 years to explain the causes of suffocations (mass death of bottom hydrobionts) developed from the first half of the 1970s on its northwestern shelf. In the same "speedy" fashion, despite more than the 100-year history of investigations in the Black Sea (the "most understood" sea in that time), only after the 10-year expedition and brain "storm" the

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unreality of outcrop and inflammation of hydrogen sulfide in its open part was, at last, scientifically based. In the 1990s this allowed to reject the adventurous project on “rescue” of population of the Black Sea countries and the sea itself from the supposed disaster through the construction of giant energetic complex for deepwater production and processing of this gas in Novorossiysk (Aizatulin and Leonov 1990).

In the early 1990s some elements of the concept of system approach to study marine basins started to develop in Russia (Photo 1.1). They included anthropogenic ecology of the ocean considering biological aspects of the issue “anthropogenic impact—marine ecosystem” (Izrael and Tsyban 1989) and geological ecology of the ocean studying “mechanisms of biosphere destruction through anthropogenic impact on relief, sediments, and suspended substance” (Aibulatov and Artyukhin 1993). The monograph “*Bases of hydroecology*” puts the greater emphasis on general issues and ideas reflecting the cause-effect relationships “environment–object” in aquatic (mainly, freshwater) ecosystem (Romanenko 2004). The book “*Scientific bases of water quality monitoring*” reviews organizational and methodological issues of foreign and national investigations on quality of continental

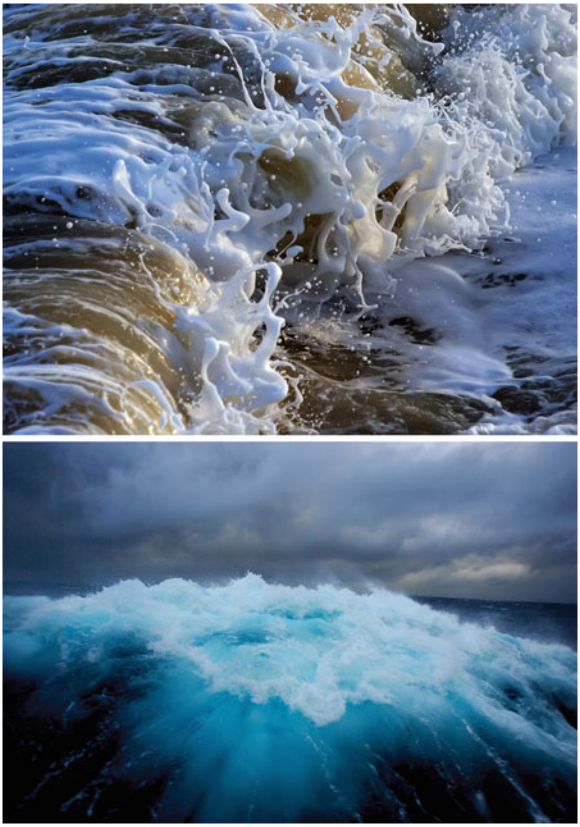


Photo 1.1 Despite the long history of investigations, the World Ocean takes time to reveal its secrets to man (by Yu. Maslyaev)

surface waters, theoretical aspects of modeling of mechanisms of its change, and problems on rating of ecological loads on water with different pollutants (Nikanorov 2005). In monograph "*Geoecological investigations on landscapes of marine shoals*" the principles of regionalization and classification of bottom landscapes, concept of stability estimation, and mechanisms of their natural-resource potential dynamics under the natural and anthropogenic impact are suggested (Mitina 2005).

Also, the examples of complex system generalization of marine ecological information for both the certain (for example, southern) seas (Keondzhyan et al. 1990; Vinogradov et al. 1992; Zaitsev 1992; Kuksa 1994, etc.) and coastal areas of the whole World Ocean (Dolotov 1996) appeared in literature. Nevertheless, all these studies addressed certainly important but partial or regional aspects of the global planetary issue- diagnosis and forecast of negative consequences of natural and anthropogenic impact on marine ecosystem state.

1.1 Marine Ecological Information

The research history of most inner and marginal seas of the World Ocean counts mostly tens of years and sometimes more than 100 years. So, the different branches of natural science accumulated a huge volume of information about regularities of functioning of single elements of marine ecosystems. Methods for obtaining and generalization of all these data are, in large extent, differed that determines their quality features. Among them the most characteristic ones are as follows:

(1) Different coverage of coastal and open areas of the sea with data; most of them are commonly referred to the more dynamic shelf zones;
(2) In most cases, large discreteness of observations in time and space;
(3) Different regularity, character (volume, structure) of observations, and methods of information obtaining, depending on professional interests, abilities, and departmental identity of observers;
(4) Multiplicity of external forcing factors and, as a consequence, large spatial and temporal variability, intricately predictable indirect and equivocal response of the sea, inaccessible for understanding without the study of ecosystem functioning mechanisms;
(5) Existence of the third coordinate (depth) in marine environment determines the essential differences in character and intensity of the same external impulses and, correspondingly, in response of abiotic and biotic components of marine ecosystem on external forcing with depth;
(6) Episodic and transient character of many natural and anthropogenic impacts determines the shortness of development of their negative consequences for the sea, which cannot be registered without continuous control system;
(7) Homogeneity of environment (only aquatic), at the first glance, simplifying the matching of ecological information, really complicates it essentially

because of the high dynamics of water mass processes (circulation structure, waving, mixing, etc.);

(8) Morphometric features of each water basin (coastal orography, bottom topography) determine the substantial spatial variability of aquatic environment response on the same external impulse;

(9) Ecological characteristics of water basin depend, in large extent, on the character of development of natural and anthropogenic processes beyond it and, not rarely, near the boundaries of corresponding watershed area;

(10) Level of generalization and data accuracy in different fields of marine science differ substantially:

- Specificity of hydrobiont life activity determines traditional quantitative generalization of biological information (assessment of stock biomass, abundance, etc.) on a basinwide basis. Only for attatched organisms (mollusks, seaweeds) or demersal fish species these characteristics are sometimes differentiated by area. Moreover, such assessments are made only in periods characteristic of hydrobionts (spawning, feeding, wintering);
- System of observations on environmental conditions existed until the 1990s (stationary network of coastal hydrometeorological stations, schemes of oceanographic stations at standard sections and ecological ranges) determined the relatively high regularity of data obtaining (daily, seasonal) and, therefore, spatial coverage of water basin with the certain type of information that allowed to make more detailed conclusions regarding the regime state both in its coastal and open areas;
- Parameters of water and bottom sediment chemical pollution in coastal zone (in the area of observations conducted by hydrometeorological service) were registered rather regularly but only at the microsurvey scale (for example, aquatory of port or bay). Just in 3–5 miles (5–8 km) from the shore this information (by expedition data) was not spread. In the open basin and areas of marine sources of pollution (drilling platforms, spoil disposals, zones of sand extraction) the observations on water pollution were carried out episodically and did not represent a system to the present day;
- Investigations on marine pollution with oil product films have very different occurrence (from one annual survey in the seas of the Arctic Ocean to 24 yearly reconnaissance flights over the Baltic Sea);
- Conclusions on sea ground pollution on the open shelf, based on materials of irregular field observations by research institutes of the Russian Academy of Science, Ministries of Geology, Fisheries, and other departments, may be authentic but only at indication of exact sampling place in each specific case;
- Monitoring of toxicological situation at the sea appears as a set of sporadic, irregular data samples (from 1 to several tens of analyses) obtained for hydrobionts caught more often in the shelf zone by coastal fishing gears (nets), in places which are the most convinient for analysts. The system of mass determinations of toxicological parameters from

commercial catches and, therefore, obtaining of statistically significant data does not exist now;
- Despite the fragmentarity of marine paleoecological and paleogeographical information, it, nevertheless, permits to trace evolution of paleobasins over millions of years and reconstruct it in perspective.

The mentioned features determine the current (very non-unique) quality level of marine ecological information, existence of blind-spots in corresponding branch of geographical science associated with its systematization, and also the need of critical attitude towards conclusions based on its analysis.

1.2 Traditional Schemes in Analysis of Marine Ecological Information

The formation of ecological situation in the sea is affected by a complex of interacting natural and anthropogenic factors. The response of marine ecosystem to external impulse is therefore indirect and ambiguous. In these circumstances:

- Results of specific investigations by different branches of marine science combined traditionally into professional or complex monographs are difficult to use for solving of contemporary problems of marine ecology. In monographs of the first type ecologically sound conclusions are often masked by methodological details, voluminous analyses, and specific terminology, which are interesting and understandable only to a narrow circle of specialists. In generalizations of the second type the complexity is formal because such publications deal usually with interesting and important but narrow special problems which are poorly interlinked among themselves;
- In the period of accumulation of ecological information the classic scheme of its generalization (structure of the typical complex monograph) was as follows: physico-geographic features of the basin-hydrological regime-hydrochemical regime-bottom sediments-hydrobiology-ichthyology. Thus, when systemizing the data, the primary attention was given to abiotic characteristics, among which it was practically impossible to select the priority parameters under such an approach. The state of hydrobiont populations, whose study allows to range external impact factors by their ecological importance, is the primary integral indicator of water basin "health";
- Traditional generalizations of data on the state of abiotic component of marine ecosystem were based on regime indices. The study of processes determining their formation, structure of the cause-effect relationships in the system "external forcing—response of marine environment—response of hydrobionts" that would allow to answer the question "why some or other events occur" tended therefore to fall by the wayside;
- Analysis of ecological importance of watershed territory for ecosystem of, for example, the Black Sea showed (Fashchuk and Shaporenko 1995; Mandych and

Shaporenko 1992) that now the contribution of basin pollution due to the direct effluents discharge by coastal plants was comparable with the similar effect from the Dnieper and Danube river runoffs. The same conclusions were made by the leading marine scientists of our country believing consentaneously that the causes of many ecological crises at the sea "lie on the coast". Nevertheless, when estimating the state of marine aquatories, today the information about watershed is included into the range of analyzed ecological data only in exceptional cases (Zaitsev 1992; Drozdow et al. 1992);

- Experience of solving of specific ecological problems in the Black Sea showed that in the contemporary context the results of one or two carefully planned (including the analysis of possible mechanisms of crisis development) directional field experiments were much more effective than the traditional long-term standard observations (Fashchuk et al. 1990; Fashchuk 1995);
- Despite the high present level of mathematical modeling and numerous examples of its use for forecasting in natural science, there is no any adequate model of marine ecosystem now. The factographic information is applicable only to statistical calculations, determination of tendencies in variations of different parameters. Its mechanical use in simulation models without understanding of nature laws does not provide practical (prognostic) result.

1.3 Geographic and Ecological Principles of Marine Ecological Data Systematization

The succession of two stages, primary accumulation of information and stage of its complex analysis, generalization, and systematization, is the objective law of natural science development. In the first half of the 1990s national oceanology found itself on the threshold of such qualitative jump. The subjective circumstances of modern times: sharp reduction in volume of field investigations and appearance of a need to solve principally new ecological problems in conditions of challenging economic situation, essentially accelerated this process.

In existing situation, the geographic and ecological approach is the most appropriate methodological principle of systematization and visualization of marine ecological information. Within a framework of this approach:

- Sea is considered as one hydrodynamic system inseparably associated with the adjacent watershed territories;
- Spatial and temporal variability of main natural and anthropogenic factors affecting marine ecosystem is assessed;
- Similar variability of the cause-effect relationships "external forcing- marine environment- state of hydrobiont populations" is considered;
- Spatio-temporal relation between evolution of marine paleobasins and their present ecological state and dynamics is traced.

The main statements of the approach are as follows:

- In parallel with conventional methods of systematization of marine ecological information, the methodology of its contemporary generalization is built on the basis of *geographic and ecological information model—"portrait" of the sea* representing a complex of ecologically significant aspects—"gingers" of the basin study by different branches of science, together with hydroclimatic, administrative-territorial, and economic features of watershed territories (Fashchuk 1997; Fashchuk et al. 1997).
- When developing model—"portrait" of the basin, the identification of priority, ecologically significant factors of external forcing and indicative factors determining stability and state of marine ecosystem is made with the use of biotic indices, whose analysis, unlike traditional approach, is carried out before the analysis of physiographic features of the basin;
- As a result of analysis of biological data, on the basis of investigations on distribution of main commercial hydrobionts and their food objects, the "centers of life concentration" representing ecologically the most sensitive to external forcing regions are defined;
- In parallel with the analysis of biological information, systematization of data on tolerance of marine organisms to pollutants and symptoms of their intoxication is carried out;
- Analysis of natural factors affecting the marine ecosystem is made not by regime indices but on the basis of *process* study, the determining ecological significance of which is established during the systematization of biological data (regime characteristics are used only for assessment of environment response to external forcing, determination of long-term trends or cycles);
- Information about forms and intensity of economic activity on marine aquatory, their distribution in space and time is a component of the geographic and ecological model—"portrait" of the basin;
- Along with natural and anthropogenic factors acting on the basin aquatory, the analyzed factors determining the state of marine ecosystem include also ecologically significant features of watershed territory;
- If the whole inner or marginal basin is studied, geographic and ecological model—"portrait" of marine ecosystem includes also information about succession of its paleobasins in geological past, based on retrospective analysis of paleoecological and paleogeographical data;—content of the "portrait" of sea (maps, diagrams, tables, descriptions) serves as a basis for development of environmental actions, recommendations on economic management, and plans of directional field experiments to study the mechanisms of crisis events in water basin;
- Based on data of directional field experiments, the simulation model experiment (drawing of scenarios of changes in natural and anthropogenic loads) for assessment of marine ecological evolutions is planned and performed.

In accordance with methodological principles of geographic and ecological modeling, the knowledge necessary for assessment of marine ecosystem state and solution of practical problems of marine ecology consists of data on factors (natural and anthropogenic) affecting the water basin and acting on its aquatory and watershed, and information about response of environment and hydrobionts to these forcing factors.

1.4 Visualization of Marine Ecological Data: Principles of Ecological Mapping of Marine Aquatories

Ecological mapping is a rather new direction in thematic geography. The geographical encyclopedic dictionary published in 1988 has not yet contained the term "ecological map" (Preobrazhensky 1990). Its origin is associated with a need of the system presentation of interrelationships between biological, social and technogenic (anthropogenic) complexes and natural (geographical) shell of the Earth, and provision of society with the demonstrative ecological information (Sdasyuk and Shestakov 1994; Smirnov and Shumova 1994).

The analysis of cartographical documents and materials published in our country since 1970 (70% of them—after 1985) made at Institute of Geography of the Russian Academy of Sciences (Komedchikov et al. 1994), has shown:

(1) Among 7 accepted groups of environmental-related maps published in this period, almost half reflects anthropogenic impact on the nature, 15% are devoted to adverse and dangerous natural processes and events, and complex ecological maps (CEM) constitute only 9%;
(2) 76% of CEMs were published after 1989 and reflected the state of terrestrial geosystems;
(3) Among the analyzed cartographic materials there was no any map reflected ecological situation on any aquatory of the Russian seas.

The author do not have the information about publication of marine ecological maps aboard during the last 10 years.

Concerning such state of things in the field of complex ecological mapping, the cartographers of Institute of Geography of the Russian Academy of Sciences absolutely fairly noticed that it was "a direct consequence of real theoretical, methodological, and methodical difficulties…. There were no yet reliable… mapping techniques, as well as techniques of studying of corresponding problems" (Komedchikov et al. 1994).

Analyzing the existing approaches to composition of ecological maps (Preobrazhensky 1990; Isachenko 1991; Smirnov and Shumova 1994), experience of development of such documents for terrestrial geosystems (Kotlyakov et al. 1990; Kochurov 1992; Kochurov and Zherebtsova 1995; Koronkevich et al. 1995), and the specificity of marine ecological information considered above, it is possible to formulate principles of ecological mapping of marine aquatories.

By their character and purpose, marine ecological maps (MEM) should be divided into 4 groups: *retrospective (paleoreconstructions), diagnostic (analytical and complex), forecasting (scenary), and general (synthetic).*

1.4.1 Retrospective Maps of Paleogeographic Reconstructions

The geological history of any marine basin in many cases may be a key to understanding of the causes of the present state of its ecosystem, an estimation of tendencies and future changes, including ecological. Thus, for example, according to paleontologic reconstruction, in Quaternary period (last 1.8 million years) the ancient basins of the southern seas were essentially transformed (Chepalyga 2002). In the Black Sea the water temperature, salinity, and species composition of hydrobionts fluctuated with the maximal amplitude (e.g., for salinity from 2 to 4‰ in the Novoevksinsky sea-lake to 30‰—in the Karangatsky basin) but the level varied slightly, and the total basin area remained almost constant.

In the Caspian Sea salinity jumps were smaller (less than 6–8‰), and the sea level changes—more essential. As a result of its periodic fluctuations affected by tectonic processes and climate change, the links between basins and with the Mediterranean via the Bosporus and Manych Straits were often broken, and the basin area increased and reduced periodically. For example, during the Khvalynsky transgression period (16–10 thousand years ago) the Caspian Sea level rose by 170–190 m (relative to the marks of previous regression), and the flooded area amounted 750,000–800,000 km^2. The cool brackish-water Early Khvalynsky Sea formed at that time, reached 950,000 km^2 by its area, i.e., 3 times more than its present area (Fig. 1.1). Salinity ranged from 6.7 to 11.5‰. Up to 20,000–40,000 m^3/s of the Caspian water flowed into the Black Sea via the Manych Strait; from the north to the south water temperature in the sea changed from 4 to 10°C.

With the beginning of Mangyshlaksky regression (9,000 years ago) the sea level dropped down to −50 m and, at some stages, down to −110 m below datum. The link of Late Khvalynsky basin with the Black Sea was discontinued. The ancient levels of the next *Mangyshlaksky* water basin were found at present depths of 75–80 m. The strongly arid climate has been established in the basin, and semi-deserts and deserts have dominated on its coast.

The shift of transgression and regression periods lasted up to 100 years was a characteristic feature of the Caspian Sea nature during the Holocene (last 20,000 years) (Kaplin and Selivanov 1999). Thus, during transgressions its total area increased by factor of 2.5 compared to the present area, and the level rose by 80 m above the current mark, reaching +50 m above datum. In the regression period the sea level dropped down to −150 m below datum.

The inclusion of retrospective maps of paleogeographic reconstructions of ancient marine basin boundaries in the geographic and ecological model of the basin is necessary for orientation of researchers and users of natural resources in the current situation. So, the position of level surface affects the distribution of areas occupied with shoal (near-mouth places), contours of its coastline, and the size and borders of habitats of commercial hydrobionts and their food objects at different stages of the life cycle (spawning, feeding).

During the peak period of last regression (1930–1942) the Caspian Sea level fell by 20 cm/year. From 1942 to 1970, in the Baku area the sea retreated by

Fig. 1.1 Quaternary paleobasins of the Caspian Sea (by Chepalyga 2002). *Dashed and continuous lines* correspond to paleo- and present boundaries of the basin, respectively

150 m for decade, and its total area was shrunk by 40,000 km^2. During the peak period (1979–1981) of the last sea transgression lasted 18 years, the rates of its level rise reached 30 cm/year. At that time, in different areas of Dagestan the mean

rates of coastal erosion and inundation ranged from 25 to 200 m/year. In coastal areas of big cities many industrial plants and constructions were destroyed and submerged, their sewage and water supply system was disrupted (Ecological Problems of the Caspian Sea 2000). In the low Kazakhstan part of the North Caspian the sea encroached upon the land within a strip of the 30 km width, and along the coastal transverse drainage lines—to even larger distance. The especially tricky situation developed as a result of submergence of the areas occupied by objects of oil and gas extraction complex and agriculture. In coastal waters of Dagestan, the content of heavy metals increased in tens times, and microbiological water pollution exceeded standard in 200 times and more.

Surely, all these problems could be avoided if users of the Caspian Sea resources were acquainted with geological history of the basin and informed of its contemporary history features.

1.4.2 Diagnostic Marine Ecological Maps

The *analytical marine ecological maps* (AMEM) may serve as visual reflection of negative response of environmental conditions and hydrobionts on external impacts, their character and intensity. With that, it is necessary to note that a set of the cause-and-effect relationships "anthropogenic impact- negative response of ecosystem" is rather extensive at a time when the number of naturally forced adverse events in the sea is rather small. Besides, the negative role of natural factors usually is either localized or experimentally not proved (though hypothetically this is beyond question), or is exceeded by heavy anthropogenic press. So, for example, in the Black Sea:

- *Upwelling and offshore-onshore currents* developing under the influence of synoptic processes at Yalta, Odessa, Novorossisk coasts are local, observed only during the summer period, persist for a short time (less than week), and their negative consequences (decrease in surface water temperature in the coastal zone) affect mainly the recreation system in these areas and do not extend on the whole coast (Photo 1.2);
- *Water exchange* via *the Bosporus and Kerch Strait* determines the supply of significant amount of pollutants into the sea, certainly influencing the ecological situation in the basin. However, by now their further fate (outside of the strait zones) and regime of pollution process remain unknown (Photo 1.3);
- Hypothetically, *intensive waves and ice formation* negatively affect the survival of hydrobionts at early stages of ontogenesis (eggs, larvae) in the areas of development of these phenomena but there is no yet specific estimations confirming these facts quantitatively and suitable for mapping;
- In the high-water years prior to the beginning of intensive economic activities the *river discharge* forming the freshening zones, served periodically as the "trigger" mechanism in array of the cause-and-effect relationships developed on

Photo 1.2 "Upwelling" phenomena, outcrop of deepwater resulting in decrease in water temperature from 24–26 to 9–12°C at the beaches during a few hours, is a characteristic feature of Yalta coast in summer under offshore winds of the north quarter (Yalta coast from the ISS. Hereinafter: photos from ISS ara courtesy of L. Desinov)

the northwestern shelf of the Black Sea (shoal down to depths of 25–40 m) in summer after the flood flow and included: *formation of extensive freshening zones → strengthening of density stratification → lessening of water ventilation in the near-bottom layer → development of oxygen deficit in topographic depressions at the bottom → temporary transition of local near-bottom hypoxia to anaerobic conditions → local death and inhibition of benthic organisms*. At present, after the involvement of powerful anthropogenic factor (eutrophication and regulation of river discharge), practically, it is not possible to distinguish the specified negative natural role of river discharge in this process (Photo 1.4);

- Along with the freshening effect and sharpening of vertical density gradients, *inflow of river waters to the sea* determines the formation of frontal zones with high horizontal salinity gradients in the northwestern Black Sea. During the spring-summer season this process also serves as "trigger" in development of another array of cause-and-effect relationships resulting in deterioration of environmental conditions. In this case, the water-mass factor—synoptic eddies (SE)—acts as "transfer" mechanism. The whole complex of relationships is realized as follows: *strengthening of horizontal salinity (density) gradients after the high-water period → lessening of stability of the Main Black Sea current (MBSC) stream → intensification of eddy formation on the coastal side of the current → development of anticyclonic circulations along the slope → lifting*

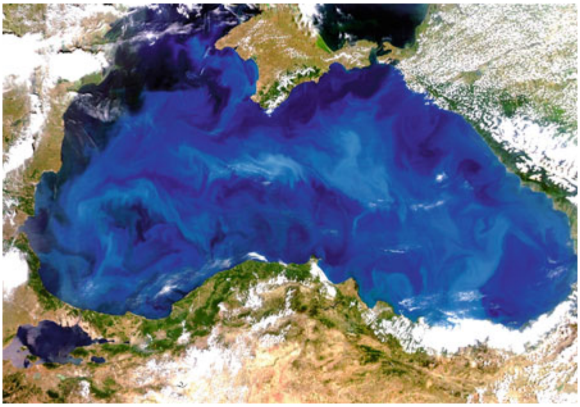
Photo 1.3 Until now the fate of toxicants entering into the Black Sea via the Bosporus has not been finally investigated (Bosporus Strait by www.cruiselog.com)

of deep waters impoverished by oxygen on their periphery and their advection onto the shelf in the zone of commercial isobaths → *change in behavior pattern of commercial concentrations of sprat (disintegration, separation from the bottom) at depths of* 70–100 m → *failure of the fish search and exploitation system.* At the same time, apart from a river discharge, other natural factors (coastal orography, synoptic situations over marine aquatory) also contribute to the SE formation. In these circumstances, it is rather difficult to discriminate a negative effect of river discharge alone;

- *Synoptic processes,* being a "trigger" mechanism, cause another complex of events during the autumn–winter period, which results in deterioration of environmental conditions in the basin. With that, the development of quasi-stationary cyclonic circulations in the open sea serves as a "transfer" link (Photo 1.5).

Photo 1.4 Regime and motion path of the Danube waters in its near-mouth area determine to a large extent the ecological situation in the region, especially during the summer (Danube Delta by www.eospan.com)

Photo 1.5 Intensity of the eastern and western cyclonic circulations in the Black Sea affects substantially not only the depth of life penetration in the basin but production potential of its waters (Black Sea by www.medina.cee.duke.edu)



The whole chain of ecological relationships looks as follows: *intensification of cyclonic activity over the marine aquatory → intensification of quasi-stationary cyclonic circulations in the open sea → strengthening of ascending movement of waters in their centers → expansion of deep hypoxia into the photic layer up to*

50 m *and above → decrease in oxygen concentration to* 2 mL/L *and less up to outcrop of deep hypoxia*. Hypothetically, it can be supposed that the results of last development stage of the specified complex of cause-and-effect relationships are negatively reflected in the life activity of cold-water forms of food zooplankton inhabiting these depths but the specific evidence for this has not been obtained yet. At the same time, upwelling in the centers of eastern and western cyclonic circulations results in an enrichment of the photic layer with mineral salts and, as consequence, favors an increase in basin productivity.

The specified events determine the fact that now the preparation of AMEMs reflecting, first of all, the adverse consequences of intensification of economic activity on marine aquatories and watersheds for water basins seems more actual and correct. With that:

- Multiplicity of the external anthropogenic impulses and cause-and-effect relationships in the marine ecosystem, arising under their influence determines the fact that number of AMEMs depends on specific water basin and may be changed with development of our knowledge about its nature, character and intensity of anthropogenic loads;
- AMEM can represent the extreme cases of development of negative events at sea, with reference to mechanism of their development and scales at the intermediate stages in its legend;
- Any analytical marine map should have the correct title containing the information on what relationships and which organisms or environmental conditions with what external impacts it reflects, and also the reference to the authors of the presented information.

1.4.2.1 Maps of Distribution of Life Concentration Centers

The well-being of marine ecosystem is determined by the state of hydrobiont populations inhabiting it. To answer a question on how the change in environmental conditions in one area of water basin or another will affect the state of commercial organism populations and their food objects, first of all, it is necessary to know a role of its various parts in formation of population abundance. This, in turn, supposes the identification of areas of their mass concentrations at different stages of biological development, or centers of life concentration. In terms of ecology, such analysis can be interpreted as defining the zones of increased “vulnerability” of commercial hydrobionts and their food objects to external impacts on the marine aquatory.

For this reason, at the next stage of development of geographic and ecological “portrait” of marine basin the biological data are systemized. The analytical marine maps of distribution of life concentration centers in marine basin serve as visual representation of this analysis.

For the long-term history of study of living resources, for example, in the Black Sea, the researchers formed a certain idea of behavior, character of distribution and abundance dynamics of hydrobionts inhabiting the basin, their response to external impacts. This knowledge was reflected in the analyzed numerous resulting monographs, dissertations, and single publications.

It emerged that along with a huge volume of collected information concerning the specified aspects of marine life, more than 160 maps of annual distribution of main pelagic commercial fishes of the Black Sea at different ontogenesis stages for the 1981–1991 period (Arkhipov 1993) were constructed, schemes of life cycles of these organisms were made, and habitat areas of main bottom commercial fishes, mollusks, and seaweeds were identified.

Nevertheless, when solving the specific ecological problems, the practical application of this knowledge is very often handicapped by its wealth, diversity and lack of proper systemization, and distribution of pelagic hydrobionts is characterized by considerable variability that makes the annual maps of this parameter of little use for application in the practical purposes.

In this connection, the vivid presentation of the specified biological information and generalization ("condensing") of corresponding cartographic material is made, using an *Integral Life Concentration Index* (*ILCI*) representing *the sum of occurrences of increased concentrations of investigated organisms in the given area divided by the number of combinations of their species and biological states*. Its mathematical expression is:

$$\mathrm{ILCI} = (1/\mathrm{N}) \sum_{j=1}^{m} \sum_{i=1}^{n} \mathrm{C}_{i,j}, \tag{1.1}$$

where $\mathrm{C}_{i,j}$—frequency of occurrence of increased concentrations of different hydrobiont species (i) in different states (j); n—number of hydrobiont species; m—number of biological states of each organism; N—number of combinations between n and m.

With use of this index, the statistical processing (Fashchuk et al. 1995) of annual distributional maps of summer-spawning (anchovy, shad for the 1981–1989 period) and winter-spawning (sprat, whiting for the 1981–1991 period) fish species at different ontogenesis stages (egg, larva, juvenile, adult), and also food zooplankton in the 0–100 m layer during the summer and winter seasons, 1985–1989 has been made (Fig. 1.2).

The introduction of term 'life concentration center', estimation, and mapping of corresponding index allowed to combine about 160 distributional maps of main pelagic fishes of the Black Sea at different ontogenesis stages and food zooplankton into 2 integral seasonal and 14 structural (for each object and biological state) maps.

The availability of these maps for investigators and natural resource users, in parallel with information on tolerance of marine organisms to oil and chemical pollution, allows, in case of catastrophic change in environmental conditions in any basin area (oil spill, toxic discharge, etc.), to assess operationally which hydrobiont species and to what degree can be affected by accident first.

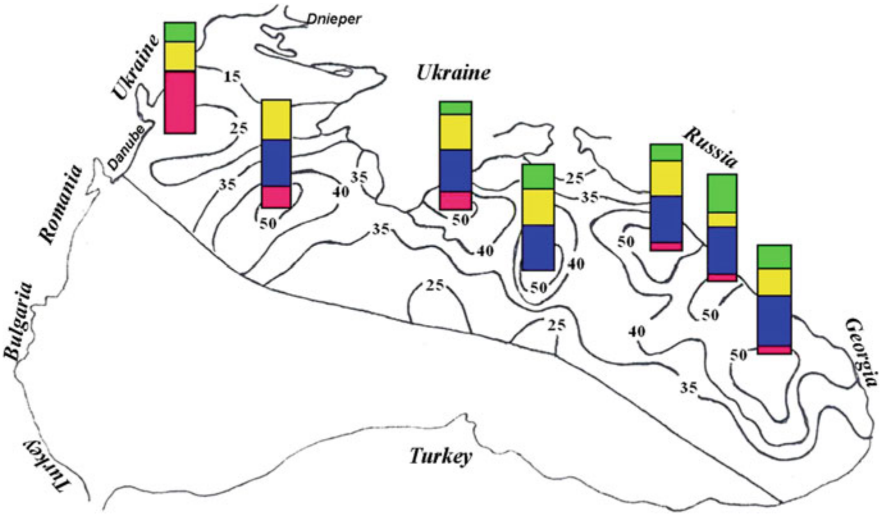


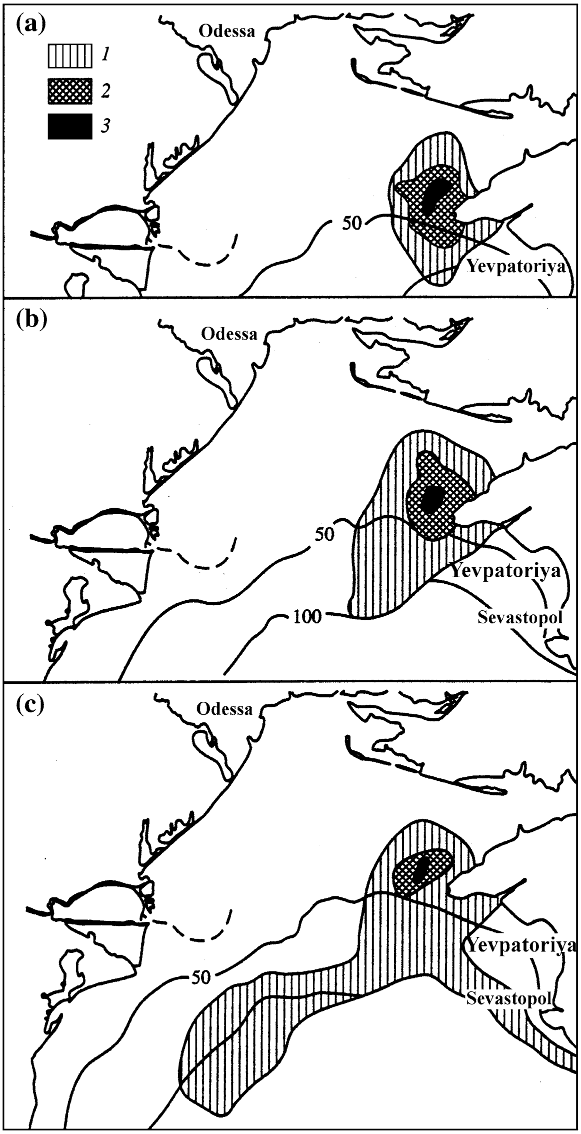
Fig. 1.2 Winter distribution of life concentration centers (*isolines*) and their structure (*diagrams*) in the Black Sea during the 1980–1990 period (Fashchuk et al. 1995). Figures on isolines correspond to frequencies of occurrence of increased hydrobiont concentrations for the period under investigation. Colours on diagrams: *red* adults; *blue* juveniles; *yellow* eggs; *green* food zooplankton

1.4.2.2 Maps of Commercial Bottom Organism Distribution

The habitation areas of commercial bottom fishes, their spawning and feeding grounds, schemes of life cycles in most regions of the World Ocean are practically stationary and well-studied. The maps of typical distribution and migration routes of commercial bottom organisms, for example, in the Black Sea allow to identify the life concentration centers in benthic zone and classify near-bottom areas of basin aquatory by their sensitivity to external impacts (e.g., Figs. 1.3, 1.4). The summary analytical Table 1.1 includes the results of systemization of data on behavioral pattern of commercial bottom organisms and their habitat conditions (Fashchuk and Sapozhnikov 1999).

In process of observations on the state of hydrobiont populations the time series of biological characteristics (biomass, stock, productivity, etc.) were formed, and tendencies in their changes were analyzed. However, taking into account shortcomings of these data (irregularity of observations in the early period of investigations, short period of regular control, etc.), such analysis can be considered only as an expert opinion of appropriate specialists, based on their knowledge of regularities of population development. Nevertheless, this information being of implicit interest for national economy and nature protection agencies does not allow to assess operatively the state of marine organism population at specific time that requires a comparison with some reference standard. In addition, its

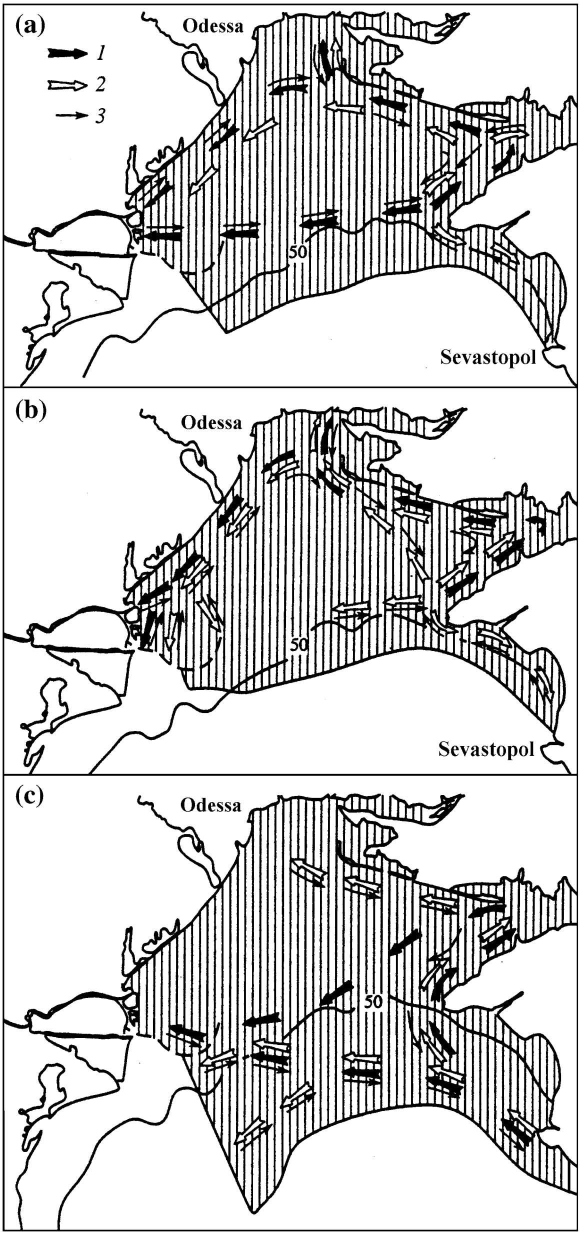
Fig. 1.3 Density of Russian sturgeon (**a**), sevruga (**b**), and beluga (**c**) oncentrations (inds./trawling hour) in November–March (Project "Seas … 1992): (*1*) ≤10, (*2*) 11–100, (*3*) >100



contemporary presentation (numerous graphs and tables) complicates the corresponding perception and assessments.

To solve this problem it is proposed to use a non-dimensional integral criterion—*index of abnormal state of biotic component of marine ecosystem* (IASB) representing the sum of normalized anomalies of biological parameters in the given year. These normalized anomalies are taken in modulus, and the anomaly sign is considered at diagram construction.

Fig. 1.4 Migration schemes of Russian sturgeon (**a**), sevruga (**b**), and beluga (**c**) in April–October (Project "Seas … 1992): (*1*) spawning, (*2*) feeding, (*3*) return migrations



Thus, the criterion expression is:

$$\mathrm{IASB} = (1/\mathrm{N})\sum_{\mathrm{i}=1}^{\mathrm{N}}\left[\left|(\mathrm{W}-\mathrm{W}_0)/\mathrm{W}_0\right|\right]_{\mathrm{i}}, \tag{1.2}$$

Table 1.1 Geography of life cycles and optimal environmental conditions for main commercial bottom species of the Black Sea

Species	Season			
	Spring	Summer	Autumn	Winter
Algae	Peak of development (down to 60 m, above 10°C))	Development (from 10–15 down to 40–60 m)	Peak of development (down to 60 m, above 10°C)	Development (from 10–15 down to 40–60 m)
Mollusks	Spawning (10–40 m) Larvae in the water column (8–13°C)	Development (10–40 m, below 24°C)	Spawning (10–40 m) Larvae in the water column (8–13°C)	Development (10–40 m, above 5°C)
Sturgeon	Spawning in the Dnieper from May. Feeding on shallows of the NW Black Sea	Spawning in the Dnieper until July. Feeding on shallows of the NW Black Sea	Spawning in the Danube until September. Feeding on shallows of the NW Black Sea	Spawning in the Danube from February. Feeding on shallows of the NW Black Sea
Sevruga	Spawning in the Danube from March. Feeding on shallows of the NW Black Sea	Spawning in the Danube until July. Feeding on shallows of the NW Black Sea	Spawning in the Danube from September. Feeding on shallows of the NW Black Sea	Spawning in the Danube until December. Feeding on shallows of the NW Black Sea
Beluga	Spawning in the Danube until June. Feeding in the Karkinitsky Bay	Feeding in the Karkinitsky Bay	Feeding in the Karkinitsky Bay	Spawning from January. Feeding in the Karkinitsky Bay
Turbot	Spawning in the Crimean coastal zone (20–60 m, 8–12°C), March–June. Eggs in the water column	Feeding on the Crimean continental slope (70–90 m). Juveniles at depths of 2–10 m	Feeding in the Crimean coastal zone (20–60 m)	Feeding on the Creimean continental slope (down to 90 m)
Mullet	Spawning throughout the sea from May. Eggs in the water column up to 100 miles from the coast. End of April (black mullet), beginning of May (golden mullet). Feeding migrations into the NW Black and Azov Seas	Spawning in the coastal zone until August. Juveniles in estuaries and river deltas (June–July)	Wintering migrations from end of September (black mullet) and beginning of October (golden mullet)	Wintering in the Crimean (golden mullet) and North Caucasian (golden and black mullets) coastal bays

where N—number of biological parameters; W—value of biological parameter i in the given year; W_0—long-term mean of biological parameter i.

It should be noted that if it is necessary and information is available, the calculation and normalization of anomalies in Eq. 1.2 can be made by any other reference parameter (e.g., parameter value in the certain year prior to beginning of economic activity or its mean value over the previous period, etc.). For the Black Sea the parameter long-term mean for the 1981–1990 period was used as reference because the similar reliable information for previous periods was not available for all components, and a comparison with the earlier post-war data would show the known picture.

Thus, with the use of IASB we have an opportunity to combine and visually present several parameters (their number is not limited, and dimension is not important) that substantially facilitates an operative assessment of abnormal state of the whole marine ecosystem and its single components The contribution (%) of each component to the total abnormality level is calculated from a simple proportion.

The example of such calculation for some biotic components of the Black Sea ecosystem is presented in Fig. 1.5. From this Figure it is clear that maximal IASB values (abnormality level) in the Black Sea during the 1981–1990 period were noted in 1981, 1984, 1986, and 1990, and minimal—in 1982. With that, in all maximum cases the positive anomalies predominated, amounting to 82, 74, 64, and 67% from the absolute value of the index, respectively.

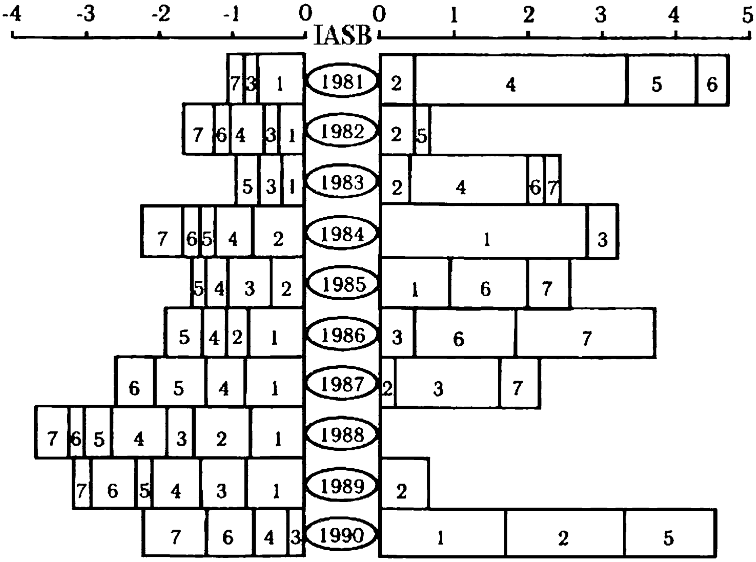


Fig. 1.5 Dynamics of the index of abnormal state (IASB) of the main pelagic components of the Black Sea ecosystem. *1–4* productivity of sprat, whiting, anchovy, and shad, respectively; *5–7* biomass (mg/m^3) of cold-water, warm-water, and non-food forms of zooplankton

The structure of positive anomalies in years of maximum varied considerably. In 1981 its components included production of shad (62%) and whiting (10%), biomass of *Calanus* (23%) and warm-water forms of zooplankton (6%).

In 1984 it consisted of sprat (89%) and anchovy (11%) production; in 1986—production of anchovy (17%), biomass of warm-water (41%) and non-food (47%) zooplankton forms; and in 1990 it included production of sprat (36%), whiting (36%), and *Calanus* biomass (28%).

The negative anomalies prevailed in 1988 and 1989, comprising 100 and 83% from absolute value of IASB, respectively. Thus, in 1988 their structure included all 7 investigated parameters almost equally, with some predominance of a fish productivity share (up to 22%). In 1989 the pattern remained unchanged, except that productivity of whiting showed a positive anomaly that year.

Passing to assessment of interannual variability in the state of pelagic components studied with the use of IASB, it is easy to determine that over the 1981–1990 period:

(1) Almost each year the productivity of sprat, anchovy, and shad was below the long-term mean. The exceptions were 1985 and 1990 for sprat, 1984, 1986 and 1987 for anchovy, and 1981 and 1983 for shad.
(2) Productivity of whiting in the beginning and at the end of the decade exceeded the long-term mean and was bew or at its level in the middle of the period (1984–1988).
(3) Biomass of cold-water zooplankton species (*Calanus)* in the beginning (1981, 1982) and at the end (1990) of the investigated period exceeded the mean long-term level, and in other years it was below it.
(4) Biomass of small warm-water zooplankton forms was continuously lower than the long-term mean from the second half of the 1980s.
(5) Biomass of non-food zooplankton forms exceeded the mean long-term level in the mid-1980s (1983, 1985–1987), and in the beginning and at the end of the decade it was below the norm.

1.4.2.3 Maps of Economic Activity Consequences for Marine Environmental Conditions

As a result of the long-term field investigations (Fashchuk 1995), it was established that the cause of development of near-bottom hypoxia and hydrosulfuric contamination zones on the northwestern Black Sea shelf consisted in parallel change in hydrological structure of its waters (deterioration of deep layer aeration) and intensification of oxygen consumption due to regulation of river discharge and change in its quality. The consequences of these processes, spatiotemporal variability of hypoxia and hydrosulfuric contamination zones, are presented on AMEM (Fig. 1.6).

The main reason of reduction of commercial mollusk and algae areas in the northwestern Black Sea is associated with deterioration of oxygen regime in the

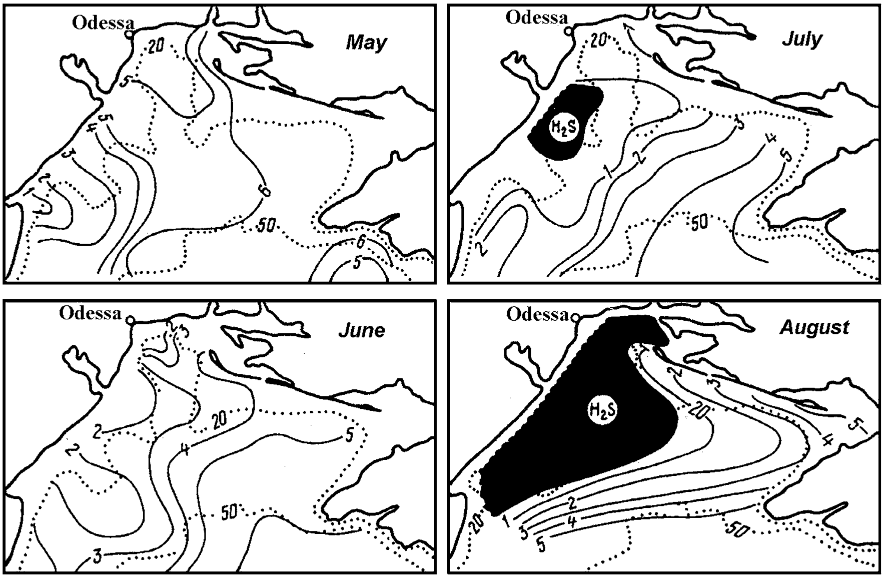


Fig. 1.6 Consequences of regulation and eutrophication of river discharge for hydrochemical regime of near-bottom water layer on the northwestern Black Sea shelf in the spring-summer period, 1990 (Fashchuk 1995). *Isolines* oxygen content, mL/L. *Dark areas* anaerobic zones with H_2S concentrations of 0.2 (July)–0.7 (August) mL/L and vertical development from 2 to 10 m (at sea depths of 8 and 25 m, respectively)

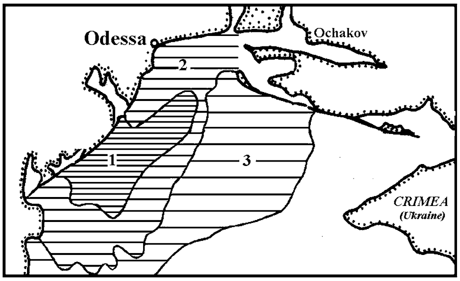


Fig. 1.7 Consequences of hypoxia and anaerobic zone development for benthic organisms of the northwestern Black Sea shelf for the 1979–1992 period (Zolotarev et al. 1996). *1* 100%-occurrence of total kill of benthic population (area—20% of the whole suffocation development zone composing about 23,000 km^2; depths—from 8 to 20 m); *2* 50–90%-occurrence (area—35% of the whole suffocation development zone; depths—from 20 to 30 m); *3* once every 2–4 years occurrence (area—45% of the whole suffocation development zone; depths >30 m)

near-bottom layer during the summer season (Zolotarev et al. 1996). The consequences of this anthropogenic factor (occurrence and scales of development of benthic fauna kill zones) on the northwestern shelf are shown on AMEMs presented in Figs. 1.7 and 1.8.

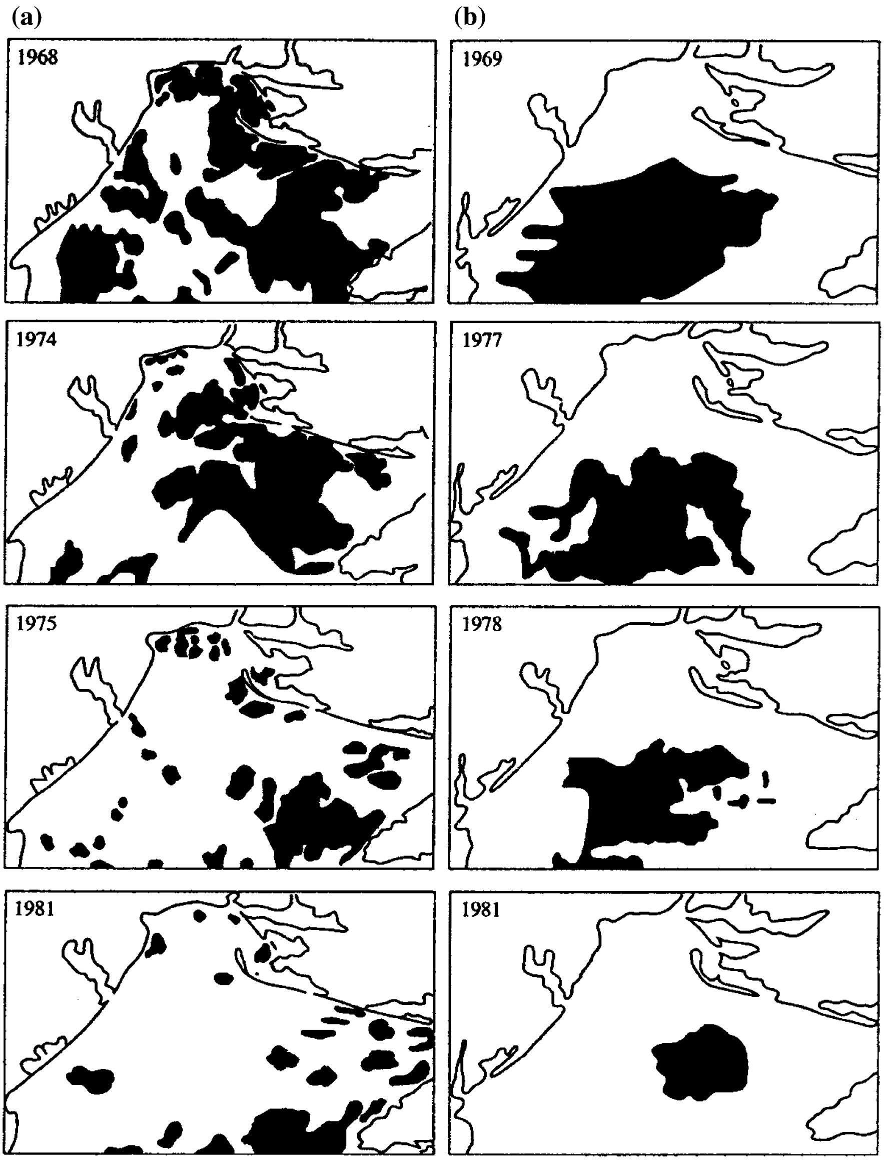


Fig. 1.8 Degradation of areas of mussel banks (**a**) and phyllophora fields (**b**) on the northwestern Black Sea shelf as a result of summer anaerobic zone development (Fashchuk 1995)

The formation of surface oil films is one of the consequences of direct sea dumping of oil products. Figure 1.9 shows the occurrence distribution of this event in the Black Sea estimated by data on its intraannual long-term aircraft monitoring (Fashchuk et al. 1996).

When analyzing the maps of Fig. 1.9, it is easy to establish that over the investigated period (1980–1990) this indicator in the northwestern Black Sea, in the Danube–Odessa area, decreased from 70–100 to 30–50% of cases a year. At the same time, the concentration zones extended, and cases of oil film registration along the coast, from Cape Tarkhankut to Sevastopol and from Sochi to Batumi, became more frequent. In the Yalta-Feodosiya, Anapa-Novorossisk, Tuapse-Sochi areas these zones were highly stable during the whole period (1980, 1984, 1986 and 1990 are illustrative).

In 1981–1990, the most stable oil film concentration zones (intraannual occurrence of more than 50%) were associated with the shallow-water areas of the northwestern Black Sea, coast from Novorossisk to Tuapse and from Sochi to Batumi, where these situations were noted annually (Fig. 1.10a). Occurrence of similar situations on aquatory from the Kerch Strait to Novorossisk and from Tuapse to Sochi was 70%, along the Crimean coast and in the open eastern sea—50%, and on the northwestern continental slope—20–30%.

The maximal interannual stability of zones with the high oil film concentration probability was registered in the Taganrog Bay and northern Sea of Azov (50–100% of cases), and its central, western, and northwestern parts were the most unharmful by this indicator. In 1981–1990 there was no any oil film concentration in these areas (Fig. 1.10b).

As a result of fishery with the use of bottom fishing gears and input of surplus amount of suspended organic matter formed after “red tides” (intensive development of phytoplankton) to the near-bottom layer, the regime of sediment deposition in the northwestern Black Sea is disturbed, and intensive mud accumulation on the bottom occurs (Zaitsev et al. 1992). The spatial scale of this event and its intensity are presented on AMEM (Fig. 1.11).

1.4.3 Complex Presentation of Marine Ecological Information

An attempt to combine the marine life elements collected in analytical maps into the complex picture on a consistent geographical basis is a natural stage of marine ecological mapping.

The mentioned specific features of natural and anthropogenic impulses, methods of collection and generalization of ecological data determine the fact that the overall distribution pattern of events unfavorable for the Black Sea and mechanisms of their development is asynchronous (timeframe, scales and duration of various crises differ substantially). In this connection, its holistic presentation seems possible only in terms of *general complex ecological schematic map*. This document combines (in form of symbols) all anthropogenic factors and their adverse effects defined in biogeosystem “portrait”. With that, the characteristics of intensity and spatiotemporal scales of loads and negative sea response are developed in legend.

Thus, if geographic and ecological model of marine basin represents a sum of main ecologically important results of investigations on its nature, the legend

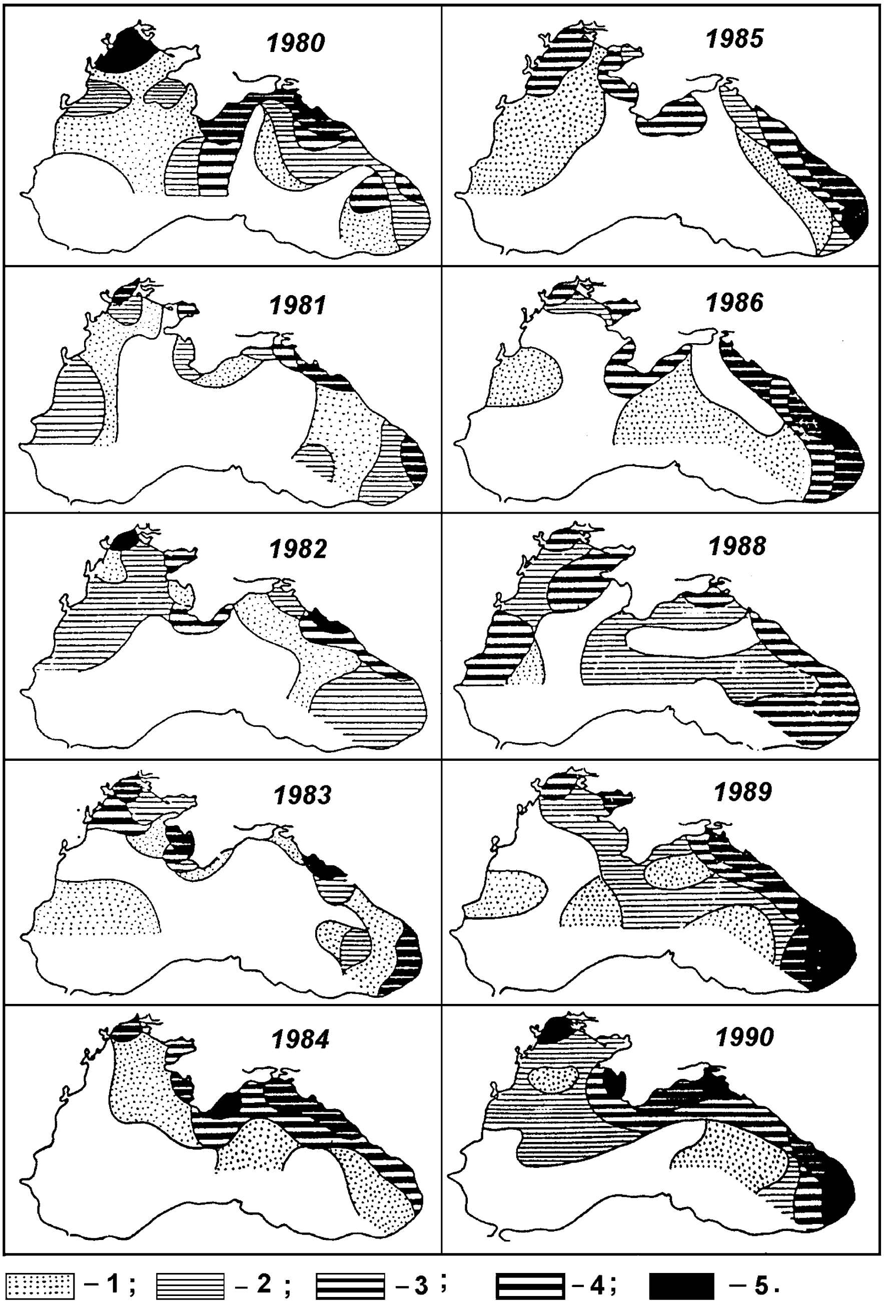


Fig. 1.9 Consequences of the Black Sea oil pollution (Fashchuk et al. 1996). Occurrence of observed cases of oil films: *1* up to 20; *2* up to 30; *3* up to 50; *4* up to 70; *5* up to 100%

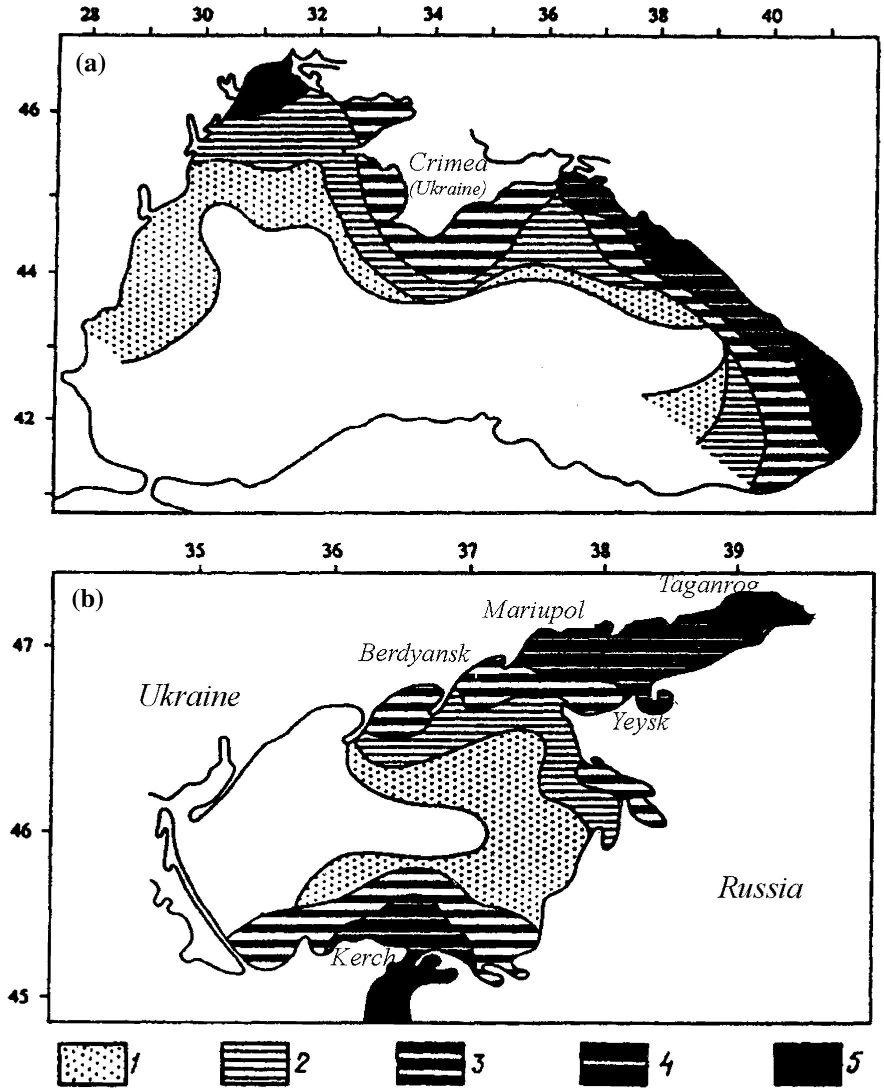


Fig. 1.10 Consequences of the Black (**a**) and Azov (**b**) Sea pollution with oil products for their surface layer during 1981–1990 (Fashchuk et al. 1996): *1–5* stability of oil film concentration zones (more than 50% of cases per year) up to 20, 30, 50, 70, and 100%, respectively

ofcomplex ecological schematic map of seais the concentrated presentation of this portrait and reflects:

- Complex of expressions portrayed on the map;
- Set of symbols used for their presentation;
- Type (contributing components) of presentational relationships 'external impact—ecosystem response';

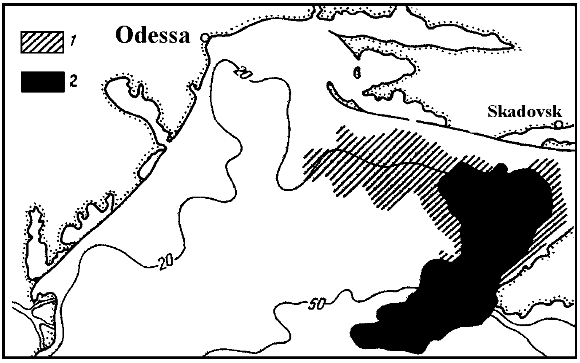


Fig. 1.11 Consequences of bottom trawl fishery and secondary pollution for regime of sediment deposition in the northwestern Black Sea for the early 1980s period (Zaitsev et al. 1992). *1* Zone of fine particles (silt deposit) distribution in the near-bottom layer (area—more than 5,000 km^2, sedimentation rate of 5–40 mm per year is by 2–3 orders higher than natural); *2* zone with silt thickness of 3–5 cm (area—3,350 km^2), including that with thickness of 30–50 cm (area—750 km^2)

- Accuracy of used data, rules of generalization and harmonization of images;
- Timeframe, depths, spatiotemporal scales of load impact and development of adverse events in ecosystem.

When assessing the marine aquatory state, the analytical and complex marine ecological maps are primarily constructed as the information concluded in them is a diagnostic basis of marine basin well-being. Now only the episodic construction of such maps is real. However, with development of the ecological monitoring system this process should become (in the future) periodic and, finally, continuous.

1.4.3.1 Integral Schematic Maps of Natural Process Development in Marine Basin

Figure 1.12 shows an example of integral schematic map of main natural processes determining formation of environmental conditions in the Black Sea and appearing priority for successful existence of main commercial hydrobionts and their food objects. It was constructed on the basis of information obtained under the analysis of biological data that enabled the identification of these factors. The schematic map allows to assess operatively the possible natural causes of abnormal marine ecological situations.

1.4.3.2 Integral Schematic Maps of Economic Activity Types on Aquatory and Watershed of Marine Basin

The results of investigations on character and types of economic activity on marine aquatory and watershed are demonstrated by integral schematic maps (Fig. 1.13)

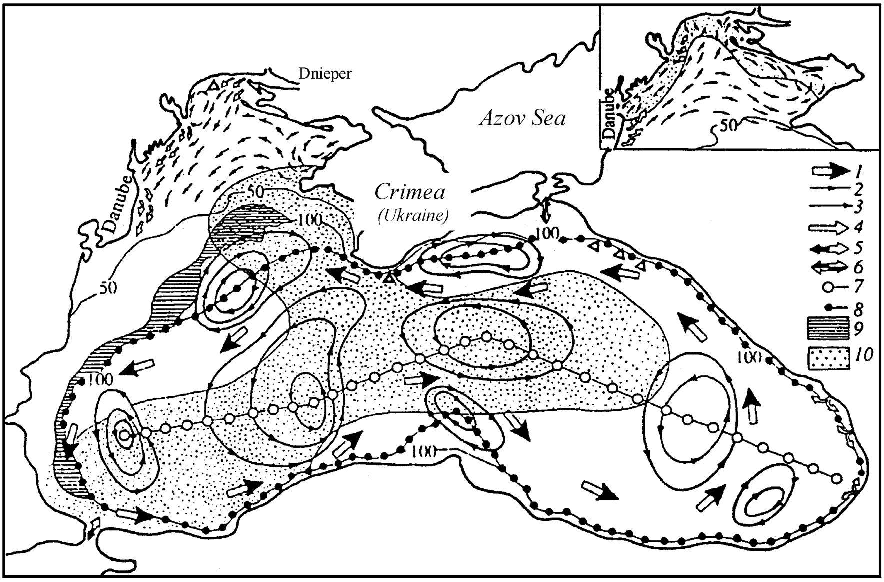


Fig. 1.12 Schematic map of main natural processes determining formation of environmental conditions in the Black Sea (Fashchuk 1997). *1* Main Black Sea Current; *2* synoptic eddies; *3* drift currents; *4* discharge currents; *5–6* exchange via straits; *7* divergence (upwelling) zones; *8* convergence (downwelling) zones; *9* areas of penetration of deep hypoxia onto the shelf; *10* areas of the maximum wave height

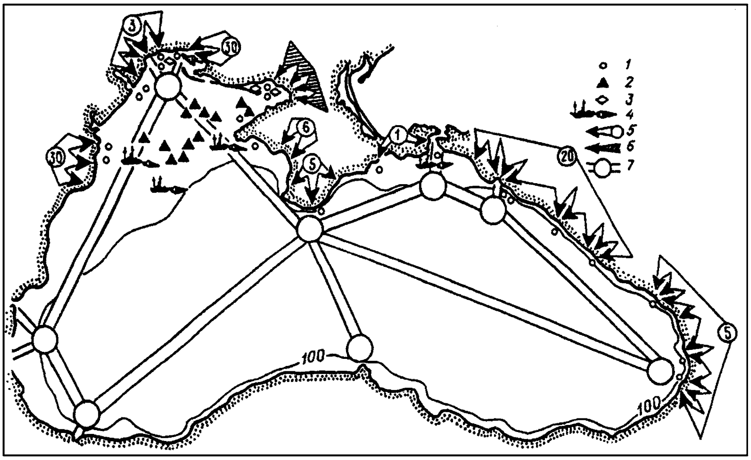


Fig. 1.13 Economic activity on the Black Sea aquatory: *1* ground dumps; *2* drilling for gas; *3* sand extraction; *4* bottom trawl fishery; *5* pollutant discharge (% from total); *6* disposal of drainage waters; *7* routes of marine transportation

allowing potential natural resource users to orientate themselves operatively at assessment of possible causes of marine ecological problems.

1.4.3.3 Integral Schematic Maps of Anthropogenic Load on Marine Aquatory and Its Consequences for Marine Environmental Conditions

When studying the scales of economic activity and its consequences for marine environmental conditions, the huge digital data sets reflecting these processes are converted into demonstrative diagrams, based on calculation of simple integral indices.

(1) For the vivid presentation and operative analysis of information about amount of pollutants entering rivers and various marine areas from different sources and for comparison of single rivers and marine areas by level of pollutant load on them the dimensionless Index of Overall Specific Anthropogenic Load of Pollutants (SALP) is proposed. For rivers its expression is:

$$\mathrm{SALP_r} = (\mathrm{Q/Nq}) \sum_{\mathrm{j}=1}^{\mathrm{N}} (\mathrm{p/P})_{\mathrm{j}}, \qquad (1.3)$$

where Q—total mean annual river discharge into the Black Sea for the investigated period; q—mean annual river discharge (km^3) for the same period; p—mean annual amount of single pollutant (t) entering the river during the investigated period; P—total amount of single pollutant (t) entering rivers; N—number of pollutants.

If in the formula 3 we replace value of Q with volume of total river discharge into the sea in specific year (km^3), value of q with volume of the investigated river discharge in this year (km^3), P with total amount (t) of the given pollutant entered the sea with river discharge for the investigated period; and p with amount of single pollutant (t) entered the investigated river in the given year, we will obtain the expression for calculation of index of the river SALP and its structure for the specific year.

(2) For shelf waters formula of the index is somewhat changed:

$$\mathrm{SALP_{sh}} = (\mathrm{S/N\,s}) \sum_{\mathrm{j}=1}^{\mathrm{N}} (\mathrm{p/P})_{\mathrm{j}}, \qquad (1.4)$$

where S—total shelf area down to isobath of 100 m (km^2), s—area of the investigated shelf (km^2); p and P are the same as for SALP$_\mathrm{r}$ but calculated for the investigated shelf area and whole shelf, respectively.

Thus, physically the SALP index represents the sum of each pollutant percentage from its total amount entered rivers or sea per unit of river discharge or unit of the investigated shelf area, respectively.

(3) For assessment of the river and sea water response to anthropogenic load in form of pollutant discharge the known conventional water pollution index (WPI) is used.

As an example of vivid presentation of information on the level of anthropogenic load on rivers and coastal areas the corresponding indices for the main rivers and shelf areas of the Black Sea were calculated, based on materials from various agencies for the 1985–1989 period, which were earlier summarized in tables with difficult access for the operative analysis.

From the diagrams shown in Fig. 1.14 it is easy to estimate operatively that, despite the larger volume of annual discharge of the Danube and, correspondingly, its prevalent contribution to the total supply of pollutants into the Black Sea, the index of overall specific anthropogenic load of main pollutants on its waters during the 1985–1989 period was lower than for the Dnieper (diagram height). Thus, in the Dnieper the loads of NH_4^+ and SS (27 and 31% from the total, respectively) predominated, while in the Danube the loads of P_{tot}, N_{tot}, and OCP (17% each) were somewhat higher, compared with other pollutants. Moreover, the specific loads of P_{tot}, N_{tot}, and OCP in the Danube were, respectively, 3, 4, and 8.5 times higher than in the Dnieper, loads of phenols and oil hydrocarbons were about the same in both rivers, and specific loads of NH_4^+ and SS in the Danube were by a factor of 2.5 and 3, respectively, lower than in the Dnieper.

The area of the northwestern Black Sea (NWBS) shelf within isobaths of 0–100 m exceeds that of the southwestern Crimean shelf in 20 times, shelf area of the South Coast of Crimea—in 40 times, and shelf areas of North Caucasus and

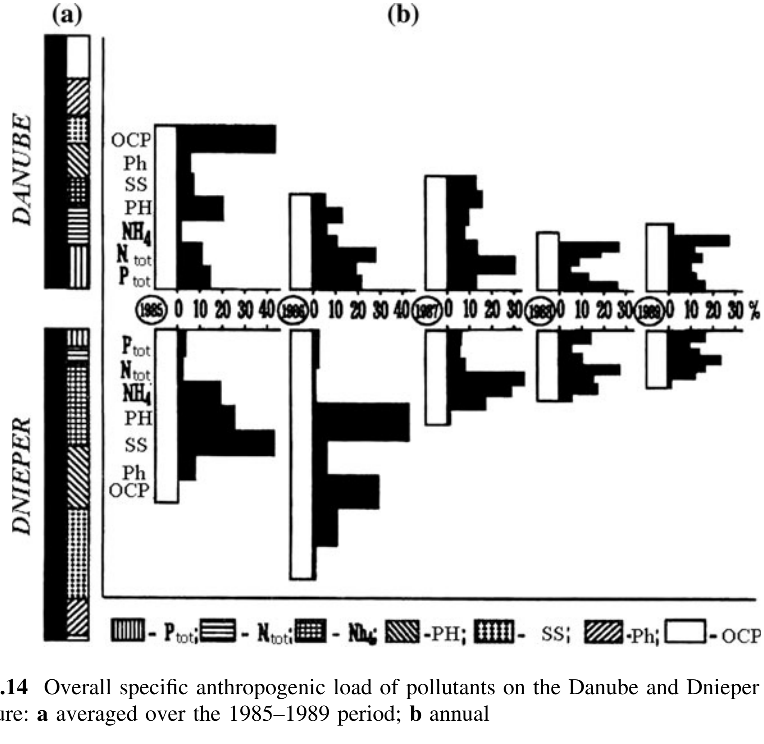


Fig. 1.14 Overall specific anthropogenic load of pollutants on the Danube and Dnieper and its structure: **a** averaged over the 1985–1989 period; **b** annual

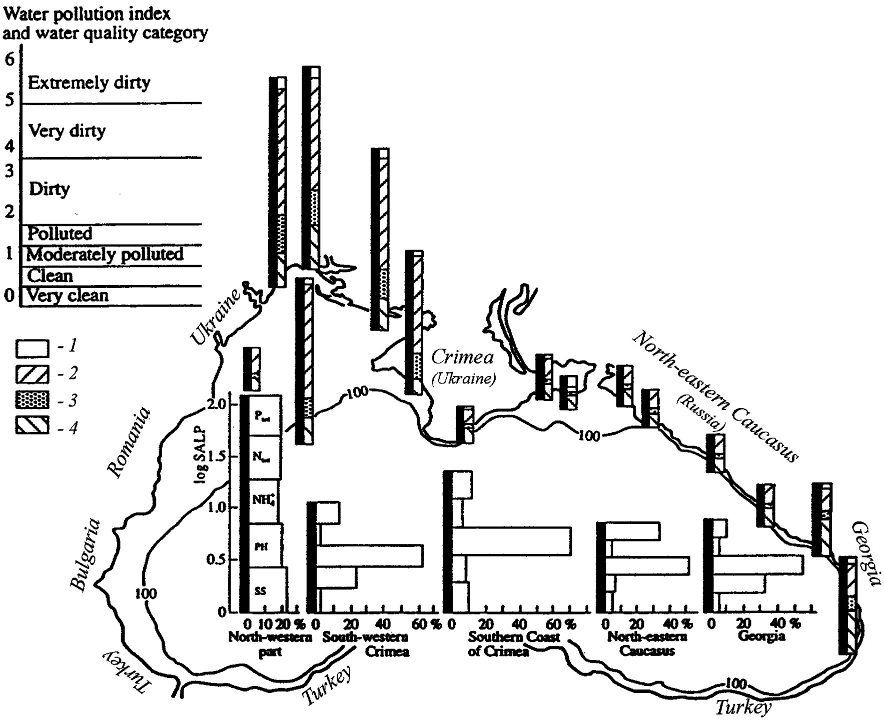


Fig. 1.15 Overall specific anthropogenic load of pollutants on surface waters ($SALP_{sh}$), water pollution index (WPI) and their structure in different regions of the Black Sea. WPI: *1* organochloric pesticides, *2* phenols, *3* synthetic surfactants, *4* petroleum hydrocarbons

Georgia—in 5 and 10 times, respectively. Nevertheless, from diagrams shown in Fig. 1.15 it is easy to estimate that its $SALP_{sh}$ is higher than in other indicated shelf areas by a factor of 9, 5, 18, and 16. The shelf of Krasnodar Territory being the second by amount of pollutant discharge from the coast and getting 20% of their total supply to the Black Sea, was the last by the $SALP_{sh}$ value.

The structure of pollutant loads varies essentially with area. In the NWBS all considered components of pollution contributed equally to SALP value (20% each). In other shelf areas the predominance of NH_4^+ in SALP was noted. Moreover, on the North Caucasus shelf the load of P_{tot} played an essential role (34%), and off Georgia and Sevastopol coasts oil hydrocarbons contributed substantially to the index value (32 and 22%, respectively). The specific weight of N_{tot} and SS in SALP on the whole shelf, except for the NWBS, did not exceed 5–8%.

Thus, the introduction of SALP criterion allowed to combine and vividly present in form of diagrams (Figs. 1.14, 1.15) a rather huge digital information containing in the complicated, lengthy summary tables, having made its accessible for operative assessment of level of pollutant load on the rivers and coastal waters, and for the analysis of specific contribution of each pollutant to its total value.

Plotting this information on the Black Sea map together with the calculated known Water Pollution Index (see Fig. 1.15), it is easy to assess simultaneously not only the level of SALP on shelf waters but distribution of their reaction (water quality) on such load by coastal aquatories.

1.4.4 Prognostic Marine Ecological Maps

Prognostic ecological maps represent the simulated results of different scenarios of possible consequences of hypothetical natural disasters or accidents under economic activity for marine ecosystems, based on mathematical modeling. As an example, Fig. 1.16 demonstrates prognostic movement trajectories of oil spot (1,500 t) after its hypothetical spill in the Kerch Strait of the Black Sea (Fashchuk and Ovsienko 2004). The calculations were made with the use of the Russian hydrodynamic model SPILLMOD (Ovsienko et al. 2005).

Using the set of simulated prognostic maps, it is easy to estimate that *for the Crimean coast of the Kerch Strait* in case of the accident oil spill of 1,500 t near its entry, pollution of beaches *under the Black Sea Current* should be expected in zones of: settlement Arshintsevo—in 24 h at east wind speed of 5 m/s; settlement Geroevskoe—in 12–14 h at east wind speed of 10 m/s; settlement Zhukovka at the exit from the Strait into the Sea of Azov—in 22 h at south wind speed of 10 m/s. *Under the Azov Sea outflow* pollution of beaches on the Crimean coast of the Kerch Strait should be expected in 24 h after spill at east wind speed of 5 m/s in the area of Cape Takil—settlement Zavetnoye, and in 10 h—at the same wind direction but its speed of 10 m/s.

For the Russian coast of the Kerch Strait under the similar accident in case of *the Black Sea inflow* oil spot will cover the Taman zone between Capes Tuzla and Panagiya in 15 h at west wind of 5 m/s, and the Cape Panagiya area—in 8–10 h at the same wind direction but speed of 10 m/s. *Under the Azov Sea outflow* pollution of these coastal areas occurs in 14 h only in case of west wind of 10 m/s.

Under other wind situations, independent of prevalent flow direction in the Kerch Strait, oil spill at anchorage on the southern entry does not threaten its coast because the spot is moved into the open sea.

1.5 Tolerance of Marine Organisms to Pollutant Impact

The information on tolerance of hydrobionts to pollutants is presented in numerous publications and overviews of Russian and foreign authors. We systematized these data for use in resolving of specific ecological problems (Fashchuk and Sapozhnikov 1999). As a result, the scheme of possible response of marine organisms at different ontogenesis stages to impact of toxicants, allowing to assess operatively the possible causes of degradation of their populations, kill of single individuals and to reveal originators of these events, was obtained.

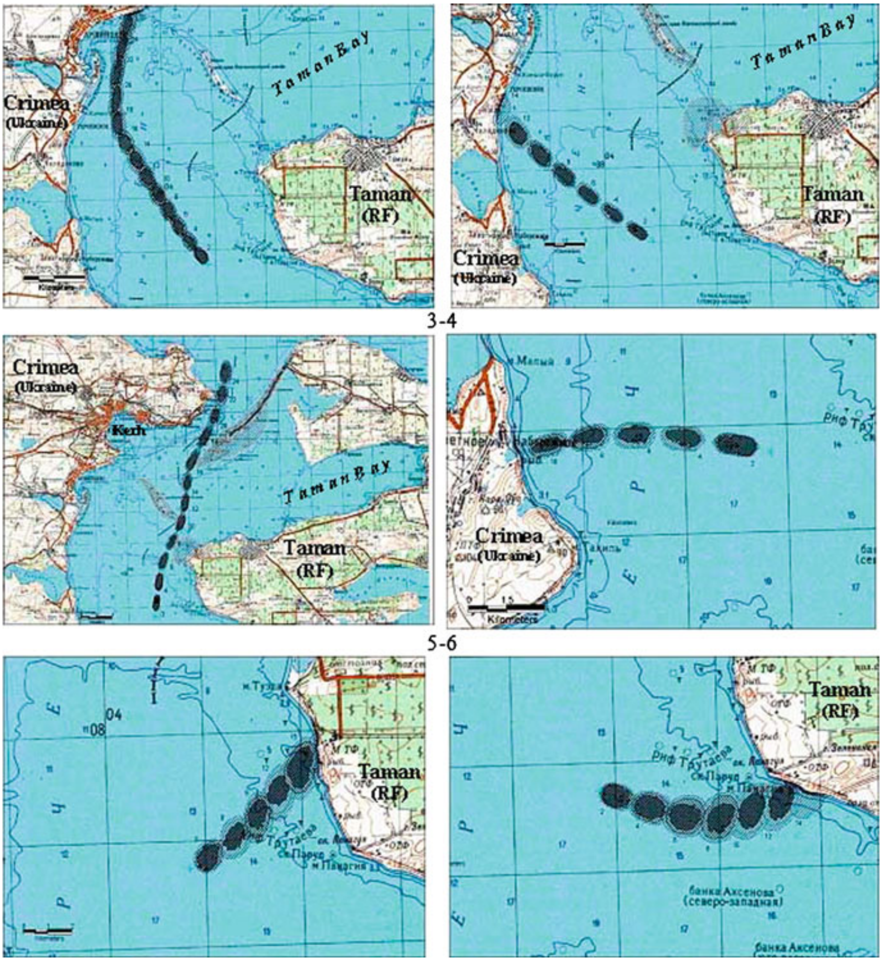


Fig. 1.16 Prognostic dynamics of spilled crude oil (1,500 t) at anchorage near the Kerch Strait entry under prevailing currents and specific wind situations. Figures on spots—time after spill. *Oil spill trajectories*: *1, 2* east wind of 5 and 10 m/s, respectively, at the coastal current; *3* south wind of 10 m/s at the Black Sea inflow; *4* east wind of 10 m/s at the Azov Sea outflow; *5* west wind of 10 m/s at the Black Sea inflow; *6* west wind of 10 m/s at the Azov Sea outflow

1.5.1 Oil Products, Phenols, Detergents

From the early 1960s, the episodic, scattered observations on impact of organic pollutants on marine organisms have become regular and task-oriented. For the next 30-year period of investigations native and foreign scientists were convinced that in different experiments the response of the same species to presence of specified toxicants in water could be quite opposite. This is explained by the complexity of specific pollutant composition which determines its ability not only to suppress but also to stimulate vital activity of hydrobionts. So oil, for example, is a multicomponent substratum by its nature, containing both toxic compounds and useful biologically active substances. "Petroleum toxin" is represented by: saturated hydrocarbons, volatile acids and phenol, organic bases, naphthenic acids (main toxicant for fish) dissolving at interaction of oil products with water. At the same time, such oil component as "growth substance" and some other compounds stimulate bioproductive processes.

The combination of such antagonistic properties determines the complexity of study of toxicity limits and threshold concentrations of organic pollutants for marine organisms. Moreover, practically there is no information on phenol influence on vital activity of hydrobionts. Obviously, this is associated with the fact that their content at sea is partly formed as a result of interaction of oil products with water, as it was mentioned above. Thus, toxic consequences of this chemical were counted at similar assessments for oil. However, considering the fact that the direct discharge with waste materials of the petrochemical, pulp-and-paper, wood industries, and public utilities is another important source of phenols in the basin, a great attention was given to studying the tolerance of marine organisms to the separate impact of this toxicant.

By character of their impact on hydrobionts oil products and phenols are similar to neuroparalytic toxins. The main symptoms and consequences of poisoning by these substances are:

(1) *Disorder of the central nervous system*—disturbance of motor reflexes and loss of orientation (intensification of chaotic motion activity with subsequent convulsions and fish death, inhibition of mollusk filterability), disturbance of utricular (balance) reflex (lateral swimming).
(2) *Disorder of physiological processes in cells*—kill as a result of hydrocarbon impact on membrane activity and other cellular and supracellular processes (damage of branchial epithelium, disturbance of structure of body organs and tissues, respiratory paralysis); change in behavioral reaction (aversion to food, loss of skins sensitivity, disorder of reproductive function and ability to attach to substratum); slowing or cessation of cell fission for microalgae.
(3) *Inclusion of oil carbohydrates in tissues of organisms, accumulation of carcinogens*—decrease in blood saturation with oxygen (asphixia); disturbance of protein balance (protein share in biomass increases); disturbance of carbohydrate metabolism in blood (decrease in content of glucose, glycogen, and lactic acid—protective system of organism becomes disorganized); disturbance of carbohydrate metabolism in liver, heart, muscles (carbohydrate content decreases); development of abnormality and loss of juvenile resilience (degradation of population).

Ranges of **toxic** (decrease in biological indicators by *50% for 2–4 days)* and **threshold** (*decrease in biological and physiologic-biochemical indicators by 50% for ontogenesis period*) oil concentrations for main species of marine organisms are presented in Fig. 1.17a (Patin 1997).

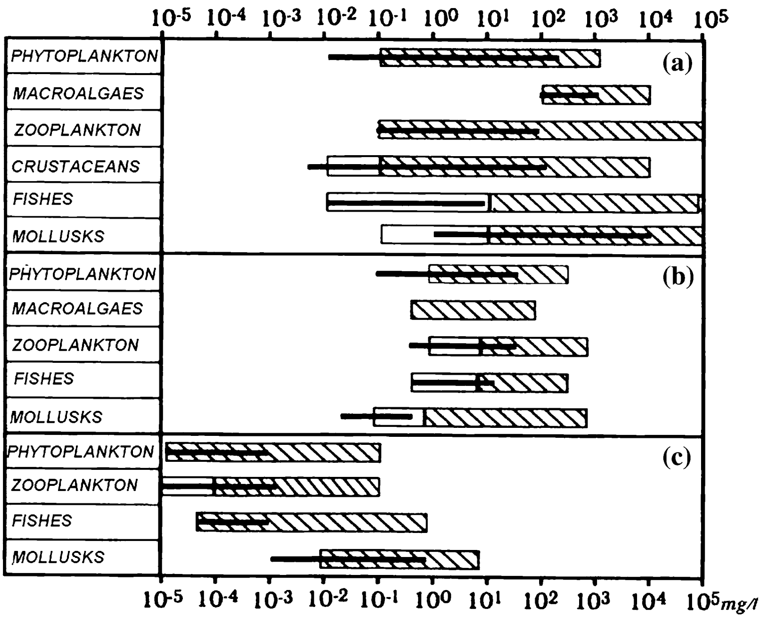


Fig. 1.17 Ranges of toxic (*rectangles*) and threshold (*bold lines*) concentrations in oil (**a**), detergents (**b**), and OCP (**c**) environment for main groups of marine organisms (Patin 1997). Ranges for early stages of development are unshaded

The results of similar analysis of data on tolerance of marine organisms to direct impact of phenols showed:

(1) Inhibition of photosynthesis for microalgaes occurred at toxicant concentrations of 10–15 mg/L, and cessation—at 600–700 mg/L. Green algaes are the most resistant, blue-green algaes—most sensitive, and diatoms occupy intermediate position.
(2) For zooplankton larvae phenol is toxic at concentrations of 10–12 mg/L. 100% of testing larvae are killed at 125 mg/L, and their adult forms—at 70–90 mg/L, in 2–4 days.
(3) Mollusks survive phenol concentrations of up to 400–1,600 mg/L, and crustaceans—from 20 to 240 mg/L.
(4) Hatching of fish larvae is slowed at phenol concentrations of 1 mg/L, at 10 mg/L it is realized only by 50%, and at 200 mg/L hatching does not occur.
(5) For fish adults (whiting, Black Sea flounder, pickerel) phenol is toxic in concentrations of 0.1–10 mg/L.

1.5.2 *Organochlorine Pesticides*

The intensification of production and practical use of pesticides in agriculture occurred in the post-war years almost in all developed countries, was caused mainly by their high efficiency in pest and weed control and also overgrowing of ponds, water reservoirs, and channels. Thereupon, prior to the early 1950s most researchers gave their attention to study of toxic OCP impact on associated weeds, insects, and seaweeds. Only in the mid-1960s, when in deltas and estuaries of rivers of the Atlantic coast of the USA and other coastal areas the cases of "mysterious" mass kill of crabs, mollusks, and fishes appeared, this problem, danger of toxic chemicals to useful marine organisms, set one of the main sections of aquatic toxicology and found wide recognition in scientific research throughout the world.

Now more than 900 substances are used as pesticides. On their basis over 100,000 various agents were developed. Depending on their intended use, all of them are combined into 22 groups, from which the following ones, for example, are important for fish economy: (1) *Insecticides*—means of pest control; (2) *Herbicides*—means of weed control; (3) *Algicides*—means of seaweed and higher aquatic vegetation control. The data on ranges of toxic and threshold OCP concentrations for the main groups of marine organisms, obtained in laboratory conditions are presented in Fig. 1.17c.

The toxic impact of OCP on hydrobionts is similar to poisoning with neuroparalytic toxicants, and appears also in disturbance of water, salt, lipid (fatty) metabolism. Thus, its mechanism is not universal and requires special separate research on each toxicant type. The intoxication effect grows with an increase in temperature, decrease in dissolved oxygen content, and at interaction of OCP with other toxicants. The main symptoms of chronic pesticide impact on marine hydrobionts are:

(1) *Inhibition of photosynthetic activity of phytoplankton and higher water vegetation*. (2) *Abnormalreaction to external impacts*—loss of temperature preferendum (ability to choose temperature), deterioration of chemoreception (sensitivity to impact of chemicals) for fish and mollusks. (3) *Violation of defense reaction*—loss of fish ability to avoid environment with dangerous toxicant concentrations, disorder of their aggregative behavior; self-digging of mollusks in ground; use of shells by crustaceans. (4) *Change in sensitivity of sensory receptors, activity of lateral line, and skin tactile receptors*—loss of orientation ability. (5) *Disturbance of osmotic regulation*. (6) *Weakening of contraction ability of muscles*—decrease in strength and rate of attachment to substratum for mollusks. (7) *Curvature and fragility of fish backbone*—decrease in collagen content in their bodies. (8) *Loss of mollusk reproductive ability*—resorption of gonads. (9) *Lethal mutations, abnormalities, kill at early ontogenesis stages*—degradation of populations (Photo 1.6).

1.5.3 Heavy Metals

By the toxicity level for hydrobionts heavy metals (HM) are ranged as: *mercury, copper, lead, cadmium, chrome, zinc, arsenic*. Thereupon, despite their considerable

Photo 1.6 Curvature and fragility of backbone, loss of aggregative instinct for fish—only one of the many symptoms of oil and chemical intoxication of marine inhabitants (photo by V. Roy)

diversity in sea water, literary data on toxic effects of HM on marine organisms are limited mainly to the specified elements.

Toxicity of HM is determined mainly by their ability to form complex compounds, covalent links with atoms of carbon, and to participate in the oxidation–reduction reactions resulting in change in metal valence. As a result of these processes, the functioning of biologically active substances in organisms is broken, ability of trace elements to pass the biological barriers increases, and balance of microbial flora is disrupted. There are some other phenomena deteriorating their life activity.

1.5.3.1 Zooplankton

Planktonic organisms with their minimum weight and volume, and the greatest specific surface of contact with environment, are characterized by an increased sensibility to different toxicants, including HM.

Mercury

The toxic and threshold concentrations of this element for invertebrates usually make 0.1–10 μg/L. With that, crustaceans are characterized by the highest sensitivity. Depending on their species and ontogenesis stage, the value of critical Hg content in water may varied substantially. Adult *Artemia salina* individuals survive concentrations from 140 to 2,300 μg/L, and their nauplial forms are killed at concentrations by a factor of 100 lower. Small forage forms (copepods), for example *Acarcia tonsa*, are also killed at low (up to 10 μg/L) Hg concentrations in water.

Protozoa are very sensitive to impact of Hg compounds also. For example, the rate of division of some infusorians in the presence of only a few micrograms of mercury in one litre of water decreases in 3–4 times by the end of the first day of experiment.

Copper

Compounds of this element harmfully affect the representatives of all zooplankton forms. Even despite the preliminary adaptation, *Artemia salina* individuals are killed at copper concentrations of 5–10 mg/L. With that, the survival rate of *Artemia* depends on development stage: 50% of eggs are killed in 48 h at copper concentration of 30 μg/L, and adult individuals—at 12 mg/L. For protozoa, the kill of 50% of testing organisms in 24 h occurs at the Cu content from 350 to 800 μg/L. The essential changes in abundance and species composition of small zooplankton forms within 30 days after the beginning of experiment are observed already at its concentrations of 5–10 μg/L.

Lead, Cadmium, Zinc

The threshold and minimal toxic concentrations of these trace metals for most of zooplankton forms are within 10–100 μg/L. Despite an insufficient knowledge of their effects on hydrobionts, nevertheless, it is known that at the lead and zinc concentrations of 1 and 10 mg/L, respectively, the regeneration of lateral cut for protozoa is delayed. For 50% of infusorians *Stilanichia mitilis* at zinc concentration of 30–35 mg/L a twofold decrease in rate of division is observed in 24 h after the beginning of experiment, and for *Euplotes harpac* species half of individuals are killed.

With an increase in temperature, the toxic impact of Pb and Cd on zooplankton strengthens. Moreover, its resistance to these metals and zinc changes, depending on development stage. For example, for some scud species the resistance to zinc impact decreases by a factor of 5–8 in passing from adult individuals to early stages of ontogenesis.

1.5.3.2 Zoobenthos

Despite the essential uncertainty of benthic community response to presence of HM in water, their sensitivity to these toxicants decreases as: *crustaceans, mollusks, worms, bryozoans*. First two groups are of commercial importance. Because of this fact and ease of study (sedentary forms), the most investigations on the HM impact on zoobenthos are devoted to mussels, oysters, and shrimps.

Mercury

Its effects on vital activity of mollusks reveal several aspects:

(1) *Function of sexual glandsis broken* that leads to decrease or complete loss of reproductive ability.

(2) *Gill enzymes are transformed* resulting in the disturbance of carbohydrate metabolism in organism.
(3) *Filtration activity of hydrobionts decreases.*
(4) *Functioning of byssus gland* determining the ability (rate and strength) to attach to a substrate, *is broken.*

At mercury concentration of 1–10 μg/L during the first hours of experiment the rate of mussel filtration increases up to 130–150% but then, with a growth of toxicant content (100–1,000 μg/L), it does not exceed 17–20%. At concentration of 32 μg/L this parameter decreases by 50%, and for mollusk *Perna perna* the similar effect is observed at 25 μg/L.

Under the Hg concentration of 0.25 μg/L the enzyme activity (glycogen content) in gonads, muscles of foot, and gills of mussels starts to decrease. Byssus of mollusk loses its ability to attach to its substrate at 1 mg/L, and the kill of 50% of testing mussels within 96 h occurs when the mercury concentration reaches 95.5 mg/L.

Copper

For most groups of marine invertebrates the minimal toxic and threshold concentrations of copper are about 10 μg/L. The resistance of benthic organisms to toxic impact of copper varies, depending on their species. Mollusk *Busycon canaliculatum*, for example, survives the concentrations up to 200–500 μg/L, and for other zoobenthos representatives the critical value of copper concentration is 50 μg/L and lower. The survival threshold by copper for oyster *Venerupis dicussata* is 10 μg/L. The twofold decrease in filtration rate for mussel *Mytilus edulis* occurs at copper content of 0.094 μg/L, and for mollusk *Perna perna*—at 0.22 μg/L.

Lead, Cadmium, Zinc

Toxic effects of Pb and Cd on various forms of zoobenthos become apparent at their concentrations of 10 μg/L. Thus there are also considerable species and group features of organism response to these toxicants.

Half of shrimps *Crangon septemspnosa* are killed in 96 h at cadmium concentration of 0.32 mg/L, and for mussels the similar effect is observed only at 25.0–33.9 mg/L of cadmium and 195 mg/L of lead. The filtration rate of these mollusks decreases by a factor of 2 at the lead and cadmium concentrations of 3.8 and 10 mg/L, respectively, and for mollusk *Perna perna*—just at 417 and 28 μg/L. Mussels lose their ability to attach to a substrate at the Pb and Cd content of 500 and 10 mg/L.

For most representatives of zoobenthos the toxic concentrations of zinc amount 10–100 μg/L. With that, their larvae are 10–1,000 times more vulnerable, compared with adult individuals. In case of zinc concentrations of up to 50–500 μg/L, the growth rate of larvae of many mollusks decreases, and for larvae of polychaete *Capitella capitata* the abnormal forms with forked ends appear.

1.5.3.3 Fishes

The HM accumulation in fish bodies is accompanied not only with their direct poisoning but consequences appearing after a certain time (mutagenic, embryotoxic, etc.). Data on fish response to toxic impact are more numerous, compared with those on other hydrobionts. As a result of their analysis, the following notions were formulated:

Mercury

The presence of mercury in fish body affects very effectively the functioning of biologically active substances—enzymes, hormones, pigments, vitamins, etc. For this reason, 50% of testing eggs are killed on the tenth day of their staying in water with the Hg content of 0.1 μg/L, and for survived embryos the subsequent irreversible damage of egg development (embryogenesis) is observed.

As a result of poisoning of fish adults with mercury, their respiratory function is depressed, and respiratory epithelium is destructed. At mercury concentration of 5–10 μg/L, the growth rate decreases, the olfactory reflex is depressed, cellular respiration in gills and enzyme activity of liver are disturbed, and at concentration of 50 μg/L half of mullet juveniles are killed after 3–4 days of the experiment.

Toxic mercury effects on fish strengthen with an increase in water temperature, decrease in salinity, dissolved oxygen content, and pH.

Copper

At an acute effect of copper compounds on fish, the necrosis of kidneys and fatty degradation develop, cerebral hemorrhage occurs. Moreover, copper ions precipitate gill secretions, resulting in kill from choke, reduce the sensitivity of organism to other chemical compounds, i.e., resistance to external impacts, facilitating development of epidemic diseases.

The lethal intoxication of juvenile and adult fish occurs at copper concentration of more than 50 μg/L (10 MACs), and that of larvae—at 10 μg/L and more. However, shad larvae, for example, perished after hatching at the copper content of up to 1,000 μg/L, and its developing eggs did not survive the concentration of 30 μg/L.

In experimental conditions, a decrease in flounder growth rate was noted at the copper concentration of 10–100 μg/L. In experiments with rainbow trout the lessening of sensitivity and olfactory reflex was registered at concentrations of 8–200 μg/L.

Lead, Cadmium

At the general rather high fish resistance to toxic effects of these elements, the biological consequences of adult fish poisoning with compounds of Pb and Cd are in many respects similar among themselves, including:

(1) Darkening of fish skin and depression of respiration;
(2) Development of scoliosis (backbone curvature);
(3) Death of sensory and supporting cells of lateral line—loss of osmotic regulation and orientation capacities.

For marine fish the threshold concentrations of these toxicants are commonly equal to 100–1,000 μg/L (10–100 MACs).

At early stages of development, fish are more sensitive to toxic impact of Pb and Cd. Thus, the fatal case for embryos, larvae, and juveniles of many species was noted at toxicant concentrations of 10–100 μg/L, and for juveniles of trout *Morone saxatiles* the irreversible destructive effect of cadmium was observed even at its content of 0.5 μg/L. At the same time, embryos of some fish species survived at lead and cadmium concentrations up to 500–1,000 μg/L because of protective effect of egg membrane.

At the lead concentrations of up to 100 μg/L, the considerable depression of respiration for mullets is noted, and half of their testing individuals perish after 1–3 days of the experiment beginning at the Cd and Pb content of 2,000 and 4,500 μg/L, respectively. In case of the constant presence in environment with the cadmium concentration just of 3.4 μg/L, the first two generations of trout *Salvenus fontimelis* perish during spawning. Even at low lead concentrations (up to 1.3 μg/L) the long presence of fish under such conditions causes their kill owing to inhibition of blood enzymes.

Zinc

The toxic properties of zinc in water are mainly associated with its ionic forms destructing enzyme systems and single organs of fish. The presence of zinc in water in concentrations exceeding 2–3 MAC (20–30 μg/L) depresses olfactory reflex of juveniles and larvae, breaks the cellular respiration in gills and enzyme activity of liver, disturbs the functions of nephritic tissue, reduces the growth rates, changes the behavioral functions. Disturbing the osmotic regulatory function of chlorine cells, zinc destroys gill epithelium and, in concentrations close to lethal, takes the mutagenic effect on eggs and larvae of Black Sea turbot.

The acute toxic effect of zinc on adult fish becomes clear at concentrations of 100–1,000 μg/L, and for the most vulnerable stages of development (embryonic and larval) this effect is noted at 40–150 µg/L. The toxic effect of Zn on fish strengthens with an increase in water temperature and salinity, decrease in dissolved oxygen content, and in the presence of others toxicants. Data on ranges of toxic and threshold concentrations of HM for main groups of marine organisms, obtained in laboratory conditions, are presented in Fig. 1.18.

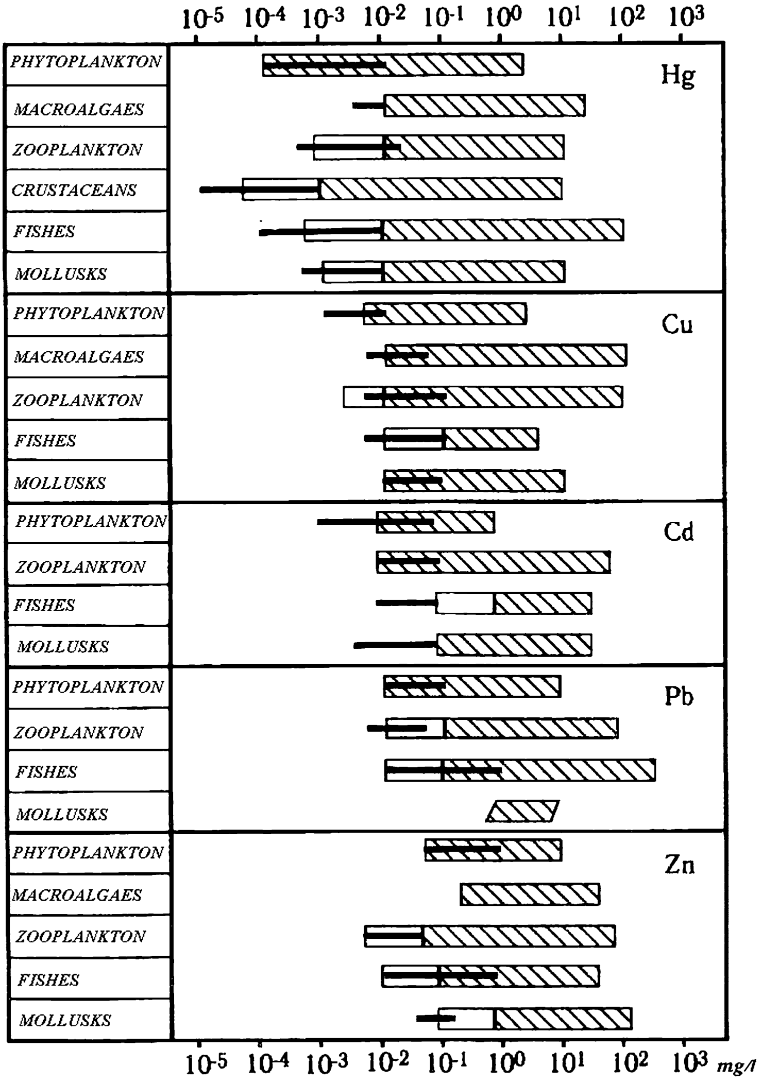


Fig. 1.18 Ranges of toxic and threshold concentrations of heavy metals for main groups of marine organisms (Patin 1997) (notations—same as in Fig. 1.17)

The established signs of hydrobiont intoxication and limits of their tolerance to hydrocarbon impact allow to identify the cases of deceases, kill, changes in behavior pattern and appearance of many commercial organisms at sea. So, for example, based on this knowledge, the causes of population degradation of many Black Sea fishes are easily explained. Their spawning grounds coincided with areas of the maximum sea pollution with oil films. As a result, fish are killed at early stages of development because at the egg and larval stage they live in the thin surface layer, being the most vulnerable to toxic effect of oil hydrocarbons.

The pollution of bottom sediments with oil products, for example, in the Sevastopol Bay reached such a level that now shad, feeding traditionally in the near-bottom layer of its coastal zone, had an “oil odor” and became almost inedible because of accumulation of monoaromatic hydrocarbons (benzene, toluene, xylene, and their derivatives) in tissues. The similar phenomenon was observed at coastal fish farms on cultivation of Atlantic salmon off the Shetland Islands in 1993, when after wreck of tanker “Braer” fish in tanks have got oil odor within several days, having lost the commercial value. Even 8 years after the wreck of tanker “Amoco Cadiz” off the French coast (1978), the coastal bottom sediments in the area of oyster banks have been infected with oil, and oysters affected with tumors of digestive tract and sexual glands, have lost their reproductive capacity (Fashchuk and Ovsienko 2004).

In the oilfield areas of the North Sea the signs of abnormal development of mass commercial fish species at the embryonic and larval level have appeared. In delta of Volga the abnormalities of sturgeon embryonic development have already reached 50–100%. In the Australian coastal waters due to oil pollution from 30 to 80% of fish embryos and larvae are abnormal, while in the clean zone their abundance does not exceed 10%. Over the last decade the abundance of ichthyoplankton (eggs, larvae) living mainly in the surface layer of the Novorossisk Bay of the Black Sea in the “atmosphere” of oil pollution, has reduced by a factor of 4–8.

It is interesting that according to results of experiments, it takes Black Sea shad from a day to several weeks of staying in clean water to clear its organism of oil, and fatter fish “is washed” much more slowly than thin. French oysters and English salmons in tanks, unfortunately, could not afford such luxury as resuscitation by clean water and have been compelled to be lost.

1.6 Integral Acuteness Assessment of Marine Ecological Situation

Integral acuteness assessment of marine ecological situation is still a matter for the future. At present, the methodologies of such analysis are developed only for some indicators (toxicological, hydrochemical, hydro- and microbiological) (Danilov-Danilyan et al. 1992; Manual on Construction of Ecological Situation Maps 1992). So, at Institute of Global Climate and Ecology (IGCE) of Federal

Hydrometereology and Environmental Monitoring Service and the Russian Academy of Sciences by results of activity of hydrobiological network and long-term research of these organizations in various areas of the World ocean, in the early 1990s six qualitative biological criteria for assessment of negative consequences of anthropogenic impact and determination of affection levels of the controlled marine ecosystems, were defined (Izrael et al. 1993). They included:

- Change in the average population biomass of plankton and benthic organisms;
- Simplification of community structure, reduction of biodiversity, complete loss of some species and their replacement with more anthropogenically resistant species;
- Appearance of indicative (adapted) microflora, increase in its abundance and expansion of areal;
- Sharp reduction, to complete extinction, of macrozoobenthos;
- Appearance of invading species or mass development of some species resulting in restructuring of cenoses;
- Eutrophication of waters and associated changes in biological and chemical regimes.

Depending on development intensity of the specified processes (characterized only by qualitative indicators), the marine ecosystem state was assessed by four gradations: “stable” “transitional from stable to crisis”, “crisis”, and “catastrophic”. Using this scale, the above-mentioned authors ranged the seas washing the Soviet coasts by degree of ecosystem degradation (1991 est.) as follows (in decreasing order of change scales): the Azov, Black, Caspian, Baltic, Japan, Barents, Okhotsk, White, Laptev, Kara, East Siberian, Bering, Chukchi Seas.

Despite some one-sidedness (only biological indicators are considered), such approach to the complex assessment of marine basin ecological state still remains unique and, to some extent, gives a possibility to be oriented in the problem. Unfortunately, the poor quality of up-to-date marine ecological data, insufficiency of information, and imperfection of our knowledge of sanitary-bacteriological, medical and biological, and other aspects of negative consequences of changes in the marine nature for human life activity are now the main reason of the lack of integral criteria for acuteness assessment of marine ecological situation counting all sides of marine basin nature.

Nevertheless, when constructing the geographic and ecological information model—“portrait” of the specific sea, modern researchers will get reliable information on the character of natural processes and economic activity on its aquatory and watershed area, tendencies in its oceanological regime (possibly, yet not resulting in the adverse ecological consequences) or changes in the state of marine populations.

Such circumstances permitted to propose the concept of “*potential ecological danger*” for introduction into marine ecological practice and to define this integral index as *the sum of ecological weights of external impact factors on marine ecosystem, capable (from experience of ecological research) to lead to adverse* *changes in the state of its components*. Development of methodology for determination of ecological weight of each factor is supposed to be done in the future.

For the seas washing the coast of the Russian Federation, 30 factors of potential ecological danger were defined (Fashchuk et al. 1997). Eleven of them are related to natural features of basins:

- Intensity of cyclonic activity over sea aquatory;
- Existence of intensive wave zones;
- Impeded water exchange with open ocean and other seas;
- Variations in water balance, level;
- Water mass exchange between marine basins;
- Presence of seasonal and pronounced permanent pycnocline;
- Occurrence of ice cover or decrease in water temperature down to extremely low values;
- Development of hypoxia and anaerobic zones in near-bottom layer;
- Disturbance of salinity regime, development of extensive surface freshening zones after extreme floods;
- Geomorphological features of coast (embayment, character of relief, intensity of abrasion);
- Bottom relief features (existence of depressions, rises);

Nineteen factors reflect the intensity of anthropogenic impact on marine ecosystem:

- Reduction of river discharge;
- Intraannual redistribution of river discharge;
- Deterioration of river water quality;
- Discharge of pollutants from coast;
- Bottom trawl fishery;
- Use of other fishing gears;
- Development of aquaculture;
- Intensive navigation;
- Ground dumping;
- Dumping of solid toxic and radioactive wastes;
- Dumping of liquid radioactive wastes;
- Development of solid commercial minerals;
- Oil and gas extraction;
- Presence of oil and gas pipelines and terminals;
- Recreation;
- Tanker wrecks;
- Wrecks of atomic vessels;
- Existence of ecologically dangerous plants in coastal zone;
- Nuclear tests.

For the integral assessment of marine ecosystem state the ratio of the obtained index of potential ecological danger to the complex index “*ecosystem response* *to external impacts*" is used. The latter represents *the sum of coefficients of ecological significance of adverse change indicators in the state of marine ecosystem components*. The development of methodologies for determination of these coefficients for each component is supposed to be done in the future. The indicators should include (in addition to the above-considered six biological factors):

- Development of mutagenic microorganisms;
- Development of cancerogenic microorganisms;
- Development of pathogenic bacteria;
- Water pollutant content in water exceeding maximum allowable concentration (MAC);
- Ground pollutant content exceeding geochemical background;
- Pollutant content in hydrobiont bodies exceeding maximum allowable level (MAL);
- Water radionuclide content above natural background;
- Radionuclide content in bottom sediments above background;
- Radionuclide content in hydrobiont bodies above MAL;
- Fish deceases;
- Appearance of mutant species.

Thus, the suggested index reflects a degree of realization of potential negative external effects in the basin and may indirectly evidence the level of integrated negative transformation of marine ecosystem, and consequently, acuteness of ecological situation.

1.7 Ecological Importance of Watershed Territory for Marine Aquatories

The ecological importance of watershed territory for marine aquatories is determined by the sum of indices reflecting its physico-geographic, politico-social, and economical features which should be a component of geographic and ecological model—"portrait" of marine basin.

1.7.1 Hydrologic and Climatic Characteristics of Marine Watershed Basin

At assessment of watershed territory, a complex of indices determining rate, volume, and timeframe of pollutant supply to the sea is integrated into the geographic and ecological model. It includes: river net characteristic, watershed area, precipitation and snow melting regimes (Photo 1.7).

For the Black Sea, for example, from the whole watershed area of 1,874,904 km^2 the Danube drainage basin constitutes 44% (817,000 km^2), that of

Photo 1.7 Hydrological events on the marine watershed basin determine to a large extent dynamics of ecological situation in near-delta areas of the sea (Flood in California by aquafornia.com)

the Dnieper—27% (505,810 km^2), the rivers of Turkey—14% (259,550 km^2), the Georgian rivers (75,000 km^2), Dniester (71,990 km^2), and Southern Bug (68,000 km^2)—4% each. Only 3% of the Black Sea watershed area including the Crimean, North Caucasian, Romanian, and Bulgarian coasts, some areas of Ukraine and Turkey, have the insignificant river discharge. Taking into account that water exchange with the Sea of Azov is of a great ecological importance for the Black Sea, when analyzing the features of its watershed, the appropriate information on the Azov watershed including the Don and Kuban drainage basins and amounting about 500,000 km^2 was considered also (Fashchuk 1998).

1.7.1.1 River net

River net of the Azov-Black Sea watershed territory includes about 1,000 large and small rivers. Most of them pertain to the Danube, Dnieper, Dniester, Don, and Kuban drainage basins (Fig. 1.19).

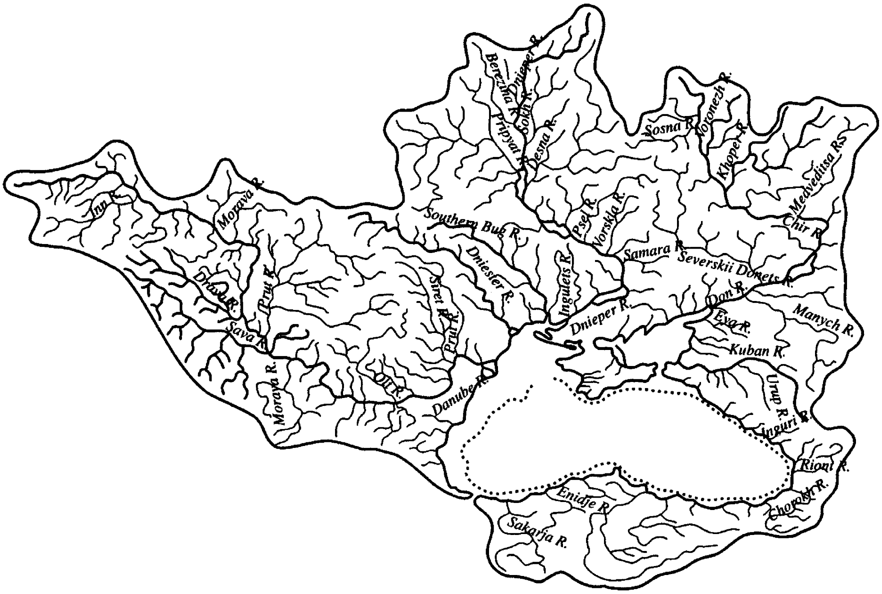


Fig. 1.19 Boundaries and river net of the Azov–Black Sea watershed territory (Fashchuk 1998)

The following characteristics of these rivers are ecologically important for the sea.

(1) *Danube*. The river length is 2,850 km. The Upper Danube (from the Black Forest to Vienna) is a purely mountain river, drainage system of which includes the *Swabian–Bavarian Highland* and narrowing between the Alps and *Czech Massif*. In middle section (from Vienna to Iron Gate) such river character still remains, though its drainage system there includes *Little and Great* Middle-Danube lowland separated by rocky chains and ridges. The Lower Danube (to its delta) is a typically plain river. The mean annual river discharge is 208 km^3, varying from 136 to 313 km^3.

Spring flood begins in February–April and continues until May in the upper and middle reaches and until June—in the lower reach. Over 60% of annual river discharge are in the spring period. There are two flood waves. The first one is associated with snow melting on plains, and the second is due to rains and snow melting in mountains. At coincidence of flood waves in the main Danube tributaries Drava, Tisa and Psell the big wave is formed in the Danube itself, causing wide overflowing in its lower current (Table 1.2).

(2) *Dniester*. The river length is 1,328 km. Its major runoff volume is formed on the northern Carpathian slopes. The mean annual runoff is 10.2 km^3, ranging from 5.36 to 19.3 km^3. In upper reaches (to Halych) this is a typically mountain river, its width there does not exceed 40 m. Downstream of Mogilev-Podolsky the river valley widens up to 2 km but in the area of branches of the Volhynian—Podolian Upland it narrows again to 200 m. Near city Dubossary the river is dammed,

Table 1.2 Hydrological characteristics of the Danube tributaries, ecologically important for the Black Sea

River	Length (km)	Mean annual runoff, (km^3)	Area of drainage basin (km^2)	Period of maximum runoff
Drava	749	19.24	40,400	Spring
Tisa	966	25.5	157,000	Spring
Sava	940	52.67	95,000	Spring
Olt	709	5.05	25,000	Spring
Siret	726	5.83	45,000	Spring
Prut	967	2.18	27,500	March–May

creating water-storage reservoir with the total area of 68 km^2 (total capacity—0.5 km^3, useful capacity—0.2 km^3). Downstream of Dubossary, within the Prichernomorskaya lowland, the river valley extends to 8 km.

Within the Carpathians the Dniester is abundant. The runoff depth reaches 800 mm there, and in lower reaches of the river it decreases to 40–50 mm, averaging 145 mm a year. Because of runoff withdrawal during the last 20 years a steady decrease in water content of the Dniester is noted. The water regime of the river is variable. There are frequent rain floods in summer, and snow and rain floods in winter. More than 40% of annual river runoff occurs in the spring season.

(3) *Dnieper*. The river length is 2,201 km. A major part of its runoff is formed in forest zone (from Valdai Hills to Kiev), which occupies more than a half of the river basin area. There the main tributaries Pripyat, Berezina, Sozh, Desna join the Dnieper.

From Kiev to Kremenchuk the river flows in forest-steppe zone and then, to its fall into the sea, in steppe zone. There the main tributaries of the Dnieper are Psel, Vorskla, Samara, Inhulets.

The water content of the Dnieper ranges from 220 mm in upper reaches to 25–30 mm in lower reaches. More than 80% of its mouth discharge is formed in the drainage basin area upstream of Kiev.

The mean annual river discharge is 47.9 km^3, varying from 23 to 83.2 km^3. Snow feeding prevails in the most part of its drainage basin. In upper reach it makes about 50% (rain and underground feeding—20 and 30%, respectively), and in the southern steppe zone, against a background of complete disappearance of rain feeding and decrease in underground feeding to 10–15%, its share increases up to 85–90%.

In upper reaches of the Dnieper the spring high water (mid-March—beginning of May), summer low water, regular autumn floods, and steady winter low water are pronounced. In tributaries of middle reach of the Dnieper (forest-steppe zone) the spring high water is more contrast. In the steppe zone of the Dnieper basin almost the whole annual runoff occurs in the spring—early summer period, and in the rest of the year the rivers run dry there.

Regulation of the Dnieper runoff by a cascade of reservoirs with the total useful capacity of 20 km^3, determined the fact that in dry years the Kiev, Kremenchuk, Dniprodzerzhynsk, Dnieper, and Kakhovka "seas" could hold the whole volume of its spring high water, and in other years—about half of it. Thus, now the regime of the Dnieper water inflow into the sea is largely determined not by natural processes but regime of water discharge through dams. Moreover, discharged river water has quite different quality. When accumulating in reservoirs, the essential changes in its properties occur (conversion of mineral forms of compounds into organic, settling of coarse fractions of solid runoff, dissolution of suspended material, etc.).

(4) *Don*. The river length is 1,870 km. The drainage area makes 422,000 km^2. The Don basin is located within Central Russian Upland, in the forest-steppe and steppe (southern part) zone. 70% of the drainage area are occupied by croplands, thus the consequences of melioration activity for this river are maximal. In upper reaches (Tula Region) rivers Krasivaya Mecha, Sosna, Voronezh join the Don river.

In middle reach (from confluence of Bityug River to confluence of Ilovlya River) two large tributaries, Khopyor and Medveditsa, join the Don River. In upper part of its lower reach Tsimlyansk Reservoir is located, with total area of 2,700 km^2, total capacity of 23.8 km^3, and useful capacity of 11.5 km^3. The Chir River flows into it. Downstream of reservoir the Don is joined by rivers Seversky Donets, Sal, and Manych.

When running into the Taganrog Bay of the Sea of Azov, the Don forms delta. In its middle part main river bed separates into two arms: left—Staryi Don, and right—Bolshaya Kalancha, with many shallow channels detached from them.

The water regime of the Don in the near-delta area (up to 140 km from delta) is affected by offshore-inshore events, especially in the low water period. Spring flood continues 1 month and more in upper reach, and about 2 months in its lower reach. Autumn rain flood is pronounced only in upper reach. Freeze-up begins in November. Breakup of ice usually occurs in March–April. The mean annual runoff of the Don River is 29.49 km^3.

(5) *Kuban*. The river length is 870 km. The area of its drainage basin amounts 57,900 km^2. Its source is located on slopes of Mount Elbrus. The river has glacial feeding. Downstream of city Nevinnomyssk it flows across the Kubano–Priazovskaya lowland and runs into the Temryuk Bay of the Sea of Azov. The main tributaries are the Malyi and Bolshoi Zelenchuk, Urup, Laba, Belaya, Pshish. The mean annual runoff is 12.39 km^3. Summer high water and single floods as a result of glacier melting and rains are characteristic features of the river. In middle reach the Krasnodar Reservoir is located.

The similar analysis was made for the main tributaries of large rivers of marine watershed basin also. Its results are presented in form of summary table. For example, for tributaries of the Danube, the largest river of the Black Sea watershed basin (see Table 1.2).

1.7.1.2 Mean Annual Runoff Depth

The geographical position of marine basin, character of river net, spatial scale and topographic features of its watershed territory determine the essential diversity of processes forming regime of river discharge from its surface, and, consequently, indirectly characterize the intensity and regime of pollution supply from land to sea. For example, the distribution of mean annual runoff depth in watershed territories of the Black and Azov Seas allows to assess operatively, what river and what coastal area are the most vulnerable to consequences of economic activity at coast by natural and climatic reasons (Fig. 1.20).

(1) *Drainage Basin of the Danube River*. The maximal values of this characteristic (500–2,000 mm and more) are noted in the western and southwestern parts of the basin in the territories of Germany, Austria and former Yugoslavia (East Alps), in Romania (Southern and Eastern Carpathians), and in the south—in territory of Bulgaria (Balkan Mountains). Its minimal values (less than 10 mm) are registered in the eastern watershed basin (Moldova, Romania, Bulgaria) directly adjacent to the Black Sea, and also in its central part—in territory of Hungary, in zone of the Great Hungarian Plain.

(2) *Drainage Basins of the Dniester and Southern Bug*. The maximal values of mean annual runoff depths (100–500 mm) are observed in the western basins, in upper reaches of rivers (Eastern Carpathians), and minimal (10–50 mm)—in their southeastern parts, on the Prichernomorskaya Lowland directly adjacent to the Black Sea.

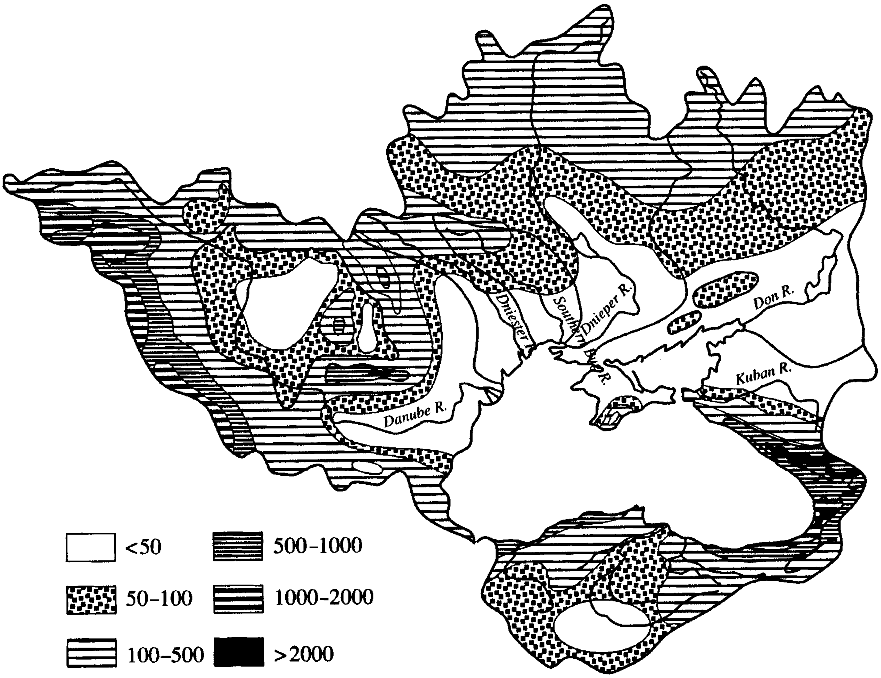


Fig. 1.20 Distribution of mean annual runoff (mm) on watershed territory of the Black and Azov Seas (Fashchuk 1998)

(3) *Drainage Basin of the Dnieper River*. The maximal runoff depths (100–250 mm) are noted in the northern basin (Polesia Lowland, Valdai Hills, Smolensko–Moskovskaya Upland, Central Russian Upland). The minimums of this characteristic are confined to the Prichernomorskaya Lowland occupying its southern part.

Watershed of the Sea of Azov including the Don and Kuban drainage basins is characterized mostly by the very low mean annual runoff (less than 10–50 mm). Only in upper reaches of the Don River (Central Russian Plain) its values slightly increase to 100–150 mm, and within the very small area on the left bank of the Kuban River (branches of the North Caucasus Mountain Range) they reach 3,000 mm.

(4) *Drainage Basins of the North Caucasian and Georgian Rivers*. The largest values of mean annual runoff (more than 2,000 mm) are found in the eastern Black Sea watershed (high-mountain and coastal areas of the Caucasus Mountains), and their minimal values (200 mm) exceeding maxima for the Don drainage basin are observed only near Anapa.

(5) *Drainage Basin of the Turkish Rivers*. On the whole Anatolian coast, from the Bosporus to the Georgian border (Pontic Mountains), the values of mean annual runoff are 200–500 mm, with an increase to 2,000 mm and more in Northeastern Turkey. In the southern Turkish part of the Black Sea watershed territory the values of this characteristic decrease to 100 mm, and in some local areas (central Anatolian Plateau)—to less than 50 mm.

1.7.2 Societal and Administrative Features of Watershed Area

The presence of the developed countries and big cities in watershed territory, urban—rural differential ratio and population density indirectly reflecting scales of communal waste water disposal from the coast, should be also considered in the geographic and ecological information model of marine basin. In this context, the most important indicators are: number of the countries (regions) in the watershed territory, their area, population size and density, urban–rural differential ratio, number and distribution of big cities, presence of rivers flowing through them.

1.7.2.1 Administrative Division

The watershed basin of the Black and Azov Seas incorporates the territories of fourteen countries (apart from the small mountain areas of Switzerland and Italy): Austria, Belarus, Bulgaria, Hungary, Germany, Georgia, Moldova, Russia, Romania, Slovakia, Turkey, Ukraine, Czech Republic, and former Yugoslavia. With that, the territories of Ukraine, Moldova, Romania, Hungary, Austria, and Slovakia are included in the Black Sea watershed zone entirely (Fig. 1.21).

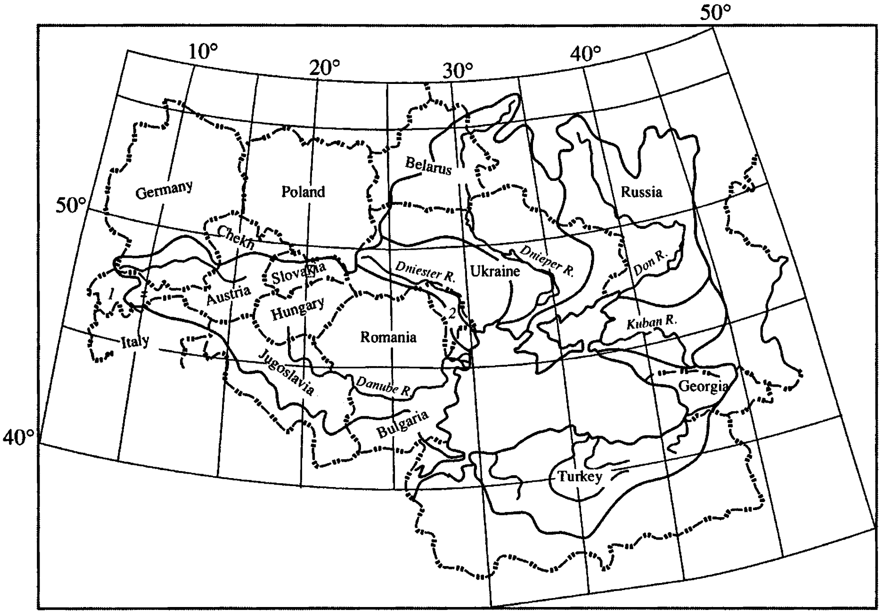


Fig. 1.21 Administrative division of watershed territory of the Black and Azov Seas. (*1* Netherlands, *2* Moldova; *solid line* boundaries of drainage basins of seas and rivers; *dashed line* state borders)

From the 15 administrative—territorial units of Russia located in territory of investigated watershed, only seven units enter into it entirely: the Smolensk, Bryansk, Belgorod, Lipetsk, Voronezh and Rostov Regions, and Krasnodar Territory. Besides, this zone also includes half of the Penza (southern part), Saratov (western part), Volgograd (western part) Regions, Kalmykia (western part), and more than half of Stavropol Territory. Only small southern areas of the Oryol, Tula and Tambov Regions are included into the Black Sea watershed basin.

The Black Sea watershed comprises also:

- Southeastern half of Belarus, including the whole Gomel Region, eastern parts of the Brest and Minsk Regions, and the southern areas of the Mogilev Region;
- Western half of Georgia;
- 40% of Turkish territory (Central and Northern Turkey);
- 70% of territory of Bulgaria (central and northern parts);
- More than 80% of former Yugoslavian territory (northern, northeastern, eastern, central parts);
- 20% of the Germany territory (southern part);
- About 40% of Czech territory (central part).

The administrative division of specific river drainage basins comprising the Black Sea watershed territory is as follows:

(1) *The Danube drainage basin*. More than half of its area are occupied by territories of Romania (237,500 km^2) and former Yugoslavia (over 200,000 km^2).

(2) *The Dniester drainage basin*. The Dniester drainage basin includes more than two-thirds of the Moldova territory (over 20,000 km^2). The remaining part (about 50,000 km^2) consists of the southern and western areas of the Odessa and Vinnitsa Regions, northern Zakarpattia Region, and southern areas of other West Ukranian Regions (Lviv, Ternopil, Khmelnitskyi, Ivano-Frankivsk, Chernivtsi).

(3) *The Southern Bug drainage basin* includes the northern and eastern areas of the Odessa and Vinnitsa Regions, central Khmelnitskyi Region, western parts of the Mykolaiv, Kirovohrad, Cherkasy Regions, and small (southern) area of the Kiev Region of Ukraine.

(4) *The Dnieper drainage basin*. More than half of its area (about 300,000 km^2) is located in the Ukrainian territory and includes the northern parts of the Lviv, Ternopil, Khmelnitskyi Regions, eastern areas of the Cherkasy, Kirovohrad and Mikolaiv Regions, northwestern and western areas of the Kherson, Zaporizhia, Dnipropetrovsk Regions, and entire Kiev, Zhytomyr, Rivne, Volyn, Chernihiv, Poltava and Sumy Regions of this country.

The remaining part of the basin (more than 200,000 km^2) comprises the Brest, Minsk, Gomel and Mogilev Regions of Belarus, and the Smolensk, Bryansk Regions and western areas of the Kursk and Belgorod Regions of Russia.

(5) *The Don drainage basin*. More than 75% of the area (about 300,000 km^2) are located in the territory of Russia and include the eastern parts of the Kursk and Belgorod Regions, southern areas of the Tambov and Penza Regions, western areas of Kalmykia, the Saratov and Volgograd Regions, and the entire Rostov and Voronezh Regions.

The remaining part of the Don drainage basin is occupied by the Ukrainian territory including the eastern and southern parts of Zaporozhia Region, and the Kharkiv, Donetsk and Luhansk Regions.

(6) *The Kuban drainage basin* occupies the western Stavporol and almost entire Krasnodar (except for the Black Sea coast from Anapa to Sochi) Territories of Russia.

The parallel use of river net scheme of drainage basin (Fig. 1.19) and Table 1.2 allows, where necessary (if consequences of accident or economic activity have reached marine aquatory), to trace possible sources (countries, regions, cities) of pollution supply from industrial discharge centers to the sea.

1.7.2.2 Population Density

More than 170 million people live in the Black and Azov Sea watershed basin. Among them:

- About 90 million people inhabit the territory of the Danube drainage basin, with half of them living in Romania and former Yugoslavia;
- More than 50 million people reside in drainage zone of the Dniester, Southern Bug, and Dnieper, from which about 40 million people—in the Ukrainian

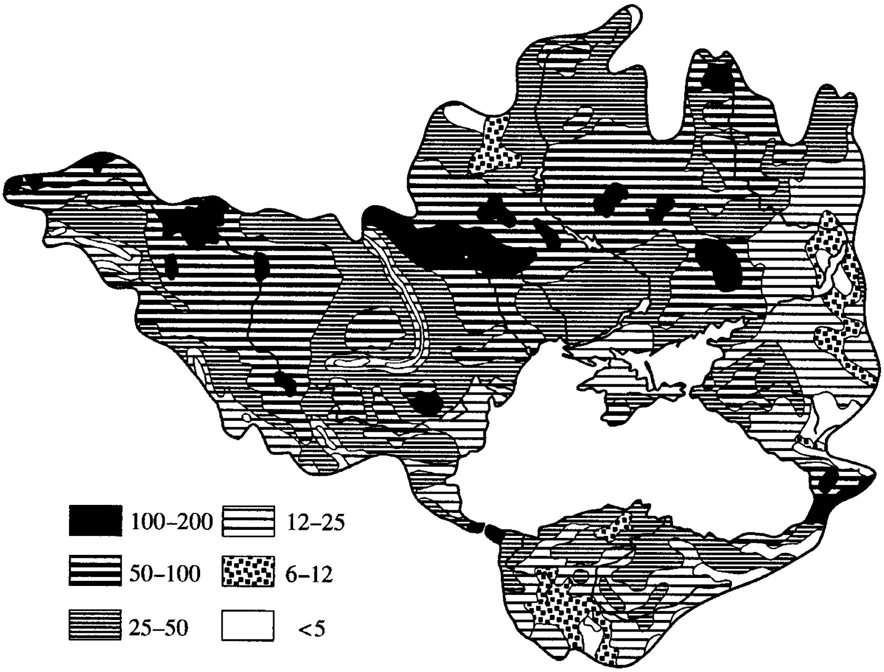


Fig. 1.22 Distribution of population density (people per km^2) in the Black and Azov Sea watershed territory

territory, about 8 million people—in Belarus, 5 million people—in Russia, and about 3 million people—in Moldova;

- About 30 million people live in the Don and Kuban drainage basin, from which more than 10 million people—in Ukraine and about 20 million people—in Russia;
- Population of drainage basins of the eastern Black Sea and Turkey does not exceed several millions people.

Population density in the watershed area of the Black and Azov Seas is distributed very non-uniformly (Fig. 1.22).

(1) *The Danube drainage basin*. The maximum values of this characteristic (up to 200 people per km^2) are noted in the areas of large industrial centers of Czechia, Austria, Germany, former Yugoslavia, Romania. Other territories of these countries occupying the most part of the Danube basin are also densely populated (about 100 people per km^2). In piedmonts of Austria, former Yugoslavia, Bulgaria, Romania, and Slovakia the population density decreases to 25–50 people per km^2, in mountain areas and lower reaches of the Danube (right bank)—to 12–25 people per km^2, and in high-mountain areas of the basin- to 6 people per km^2 and less.

(2) *The Dniester, Southern Bug and Dnieper drainage basin*. In this territory the population density maxima (up to 200 people per km^2) are observed in upper reaches of the Dniester and Southern Bug (western regions of Ukraine) and in

industrial centers of the Kiev, Cherkasy, Poltava, Kharkiv Regions of Ukraine. In local areas of the Dnieper upper reach (Belarus), middle and lower reaches of the Dniester (Moldova, Odessa Region), middle reach of the Dnieper the population density remains at high level (up to 100 people per km^2). In lower reaches of the Dnieper and Southern Bug this characteristic essentially decreases (down to 25–50 people per km^2), and in the most (left-bank) part of the Kherson Region it is only 12–25 people per km^2.

(3) *Drainage Basin of the Don and Kuban Rivers*. The maximum population density (up to 200 people per km^2) is noted in the Ukrainian territory of the basin (Kharkiv, Luhansk, Donetsk, Zaporizhia Regions), drainage areas of the Don upper reaches (Lipetsk, Voronezh Regions of Russia), middle and lower reaches of the Kuban. In middle and lower reaches of the Don, in the eastern part of the Kuban basin the density decreases down to 12–25 people per km^2, and in the left—bank part of the Don basin (Saratov, Volgograd, eastern Rostov Regions, and Kalmykia) its values are only 6–12 people per km^2 and less.

(4) *Drainage Basin of the North Caucasian and Georgian Rivers*. The greatest values of population density in this area are noticed in the territory of Georgia, 50–100 people per km^2, with the maximum (up to 200 people per km^2) in coastal zones (Batumi, Poti). In Krasnodar and Stavropol Territories forming part of the eastern Black Sea watershed, the population density ranges from 25–50 to 12–25 people per km^2, respectively.

(5) *Drainage Basin of Turkish Rivers*. In larger part of the coast of Turkey, from Trabzon to the border with Georgia, the population density is 25–50 people per km^2. Only in area of Trabzon it increases up to 100 people per km^2. In the central Turkish zone of the Black Sea watershed territory the density of population decreases to 12–25 people per km^2 and on its southern boundary does not exceed 6 people per km^2.

Almost in the whole territory of the Black Sea watershed basin the urban population prevails over rural population, with the maximal predominance (more than 70%) in Austria, Czechia, Slovakia, the Volgograd, Rostov, Saratov Regions of Russia, and the Dnipropetrovsk, Donetsk (90%), Zaporizhia, Kiev, Luhansk, Kharkiv Regions of Ukraine. The rural population prevails in all western Regions of Ukraine (more than 60%), in Moldova and Turkey (more than 50%). In other territory of the Black Sea watershed the urban–rural ratio is about 1.

The societal and administrative factors of the countries and their specific areas located in territory of marine watershed are included in summary analytical tables (e.g., Table 1.3), another component of geographic and ecological model—“portrait” of marine basin.

1.7.3 Economic Characteristics of Watershed Territory

The level of development and character of industrial production and agriculture, distribution of industrial enterprises, and technique of land resources use are very

Table 1.3 Societal and administrative parameters of countries located in territory of the Black Sea watershed basin

Country	Parameter					
	Area (thous. km^2)	Population (thous. people)	Density (people/ Km^2)	% Urban population	Industrial cities in watershed zone	Main rivers
Austria	82.73	8,000	91.7	77	Vienna, Graz, Linz, Salzburg, Innsbruck	Danube (350 km), Inn, Drava, Morava
Bulgaria	110.55	8,950	81.5	65.5	Sofia, Plovdiv, Varna, Rousse, Pernik, Stara Zagora, Pleven, Shumen, Sliven, Dobrich	Danube, Maritsa, Iskar,Yantra, Mesta, Struma
Hungary	92.34	10,679	114.3	59	Budapest, Szeged, Pecs, Miscolc, Gyor, Debrecen, Nyiregyhaza, Szekesfehervar	Danube, Tisa
Germany	244.28	6,500	251.0	92	Munich, Salzburg	Danube
Georgia	69.70	5,266	75.2	53	Batumi, Kutaisi, Poti, Sukhumi, Zestafoni, Chiatura, Tkibuli, Tkvarcheli	Rioni, Kodori, Ch'orokhi, Mzmyta, Inguri, Bzyb, Supsa
Moldova	33.70	4,185	124.2	42	Kishinyov, Belts, Tiraspol, Bender	Dniester, Reut, Bic, Botna, Prut, Chugor, Larga, Kamenka
Romania	237.5	22,900	101.0	63	Bucharest, Brasov, Constantia, Jassy, Timisoara, Galati, Cluj-Napoca, Craiova, Ploesti, Braila, Oradea	Danube, Jiu, Olt, Siret, Prut, Somes, Mures
Slovakia	49.00	5,170	94.8	74.3	Bratislava, Kosice	Danube, Vah, Hron
Turkey	769.63	5,500	72.6	45	Ankara, Samsun, Sinop, Rayseri, Sivas, Zunguldak, Trabzon, Adapazan, Eregli, Kirikkale	Yenice, Coruh, Sakarya, Kizilirmak, Yesilirmak
Chechia	78.9	10,300	76.6	74.3	Brno, Olomouc	Danube, Morava
Former Yugoslavia	255.40	25,000	93.2	48	Belgrade, Zagreb, Sarajevo, Ljubljana Novi Sad	Danube (558 km), Tisa, Sava. Morava, Drina

important for assessment of probable reasons of marine ecological crises. Technique of land resource use in the watershed basin determines to a large extent quality of river and, consequently, coastal sea waters. In this context, these factors should be considered as a component of geographic and ecological information model of marine basin.

1.7.3.1 Distribution of Land Resources and Agriculture Branches

Soil maps, maps of cropland distribution (Fig. 1.23) and data on their use, in combination with the knowledge of chemical fertilizer or chemical reagent types applied to the certain soil at cultivation of any given crop, allow also to define countries and their specific territories within the watershed basin, which represent the potential ecological danger for river and, hence, coastal sea waters (Table 1.4). Thus, it should be noted that, when identifying the areas of possible active impact of agricultural production on ecological state of marine aquatory, along with the proposed criterion (character of land resource use) it is necessary to consider the area distance from the river mouth, character of river (mountain, plain), and information on transformation rate of toxicants, mineral and organic agricultural wastes in the freshwater environment.

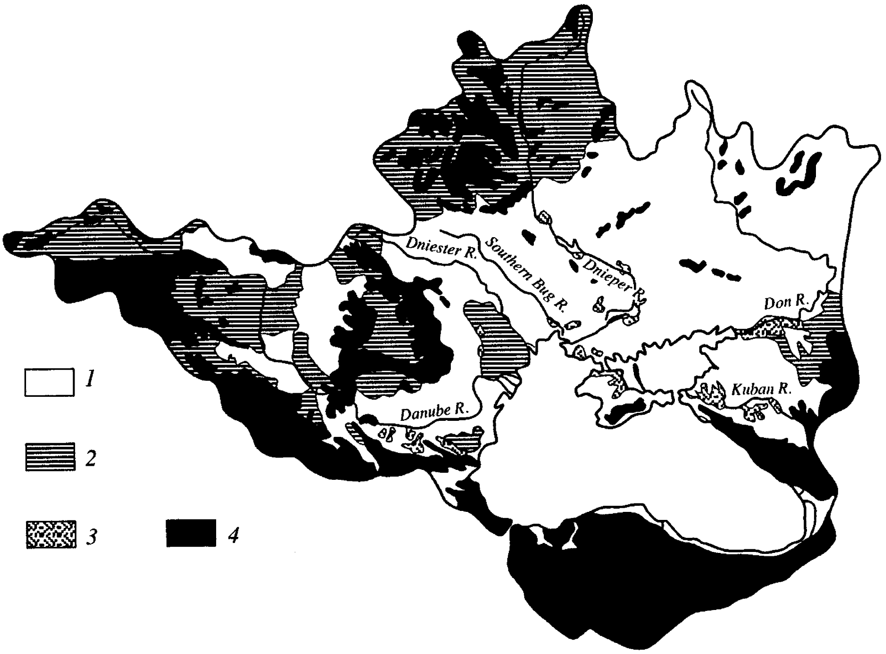


Fig. 1.23 Distribution of cropland in the Black and Azov Sea watershed basin: *1* unirrigated ploughs; *2* unirrigated ploughs with forests and pastures; *3* irrigated ploughs; *4* steppe, meadow and forest pastures, forests, forests with plough

Table 1.4 Characteristics of agricultural production in main countries of the Black and Azov Sea watershed basin

Country	Characteristics
Austria	Cropland—4.1 million ha (50% of country area): 50%—plough, gardens, vineyards, 50%—meadows, pastures. Crops: wheat, barley, sugar beet, potato, corn, oat
Bulgaria	Cropland—6.2 million ha (56%): 60%—plough, 32%—meadows and pastures, 5%—perennial crops. Acreage: cereal and leguminous crops—52%, feed crops—29%. Crops: wheat, corn, barley, vegetables, tobacco, cotton, sugar beet, berries, rose, mint, grape
Hungary	Cropland—6.5 million ha (71%): 77%—plough, 19%—meadows and pastures. Acreage: cereal and leguminous crops—64%. Crops: wheat, corn, sugar beet, sunflower, hemp, grape. Poultry breeding: hens, ducks
Georgia	Cropland—3.2 million ha (46%): 63%—hay-fields and pastures, 25%—plough. Crops: tea, citrus plants, tung
Moldova	Cropland—2.6 million ha (77%): 69%—plough. Crops: grape, fruit and berry crops, wheat, corn, barley
Romania	Cropland—15 vln ha (63%): 66%—plough, 20%—pastures, 9%—meadows, 4%—perennial crops. Acreage: cereal and leguminous crops—67%, feed crops—11%. Crops: wheat, corn, barley, grape, vegetables
Turkey	Cropland—25 vln ha (33%). Main branch—irrigated and dry cropping in costal plains and intermountain hollows. Crops: wheat, barley, corn, cotton, sugar beet, flax, nuts, fig, olives. Livestock farming: sheep, goats
Former Yugoslavia	Cropland—15 million ha (59%): 50%—plough, 45%—meadows and pastures, 5%—perennial crops. Acreage: cereal and leguminous crops—60%, feed crops—15%. Crops: corn, wheat, sugar beet, sunflower, hem, tobacco, plum, grape. Livestock sector: cattle, swine breeding

In this context, it is difficult to anticipate the essential ecological importance of even large livestock breeding complexes for marine aquatories, provided that they are located at a great distance from deltas of main rivers running into the sea. Alternatively, persistence of many toxicants used in agriculture causes the necessity to consider the probability of impact of even their most distant sources at solving of marine ecology problems, despite their possible accumulation in river bed deposits, hydrobionts and water-storage reservoirs.

1.7.3.2 Distribution and Character of Industrial Production

Untreated waste water of industrial plants located in the territory of marine watershed basins and accidents with oil pipelines are the strong sources of persistent pollutants for river waters and coastal zones of the affected seas (Photo 1.8). Depending on type of industrial production, their content in waste waters varies substantially (Fig. 1.24).

Not all industrial wastes contain substances ecologically dangerous to marine basins, and some of them contain toxicants easily decomposing in water environment. As a result of the analysis, the following conclusions were made:

Photo 1.8 Technogenic catastrophes and wasteful activity in the watershed basin territory leave their mark on coastal marine ecosystems

(1) From 15 basic industries comprising more than 300 production types, waste water of *fuel and building industry plants* (more than 20 production types) do not contain persistent toxic pollutants. *These industries do not represent ecological danger to marine aquatories*;

(2) Main toxicants in waste water of all production types of *pulp-and-paper industry* are non-conservative, easily oxidizing in water environment chlorine, methanol, and thiols (dimethyl sulfide, dimethyl disulfide). Thereupon, *waste water of this industry (provided that they are not discharged into the sea directly) does not threaten marine aquatories*;

(3) Toxic wastes of some *petrochemical* (extraction of aromatic hydrocarbons), *chemical* (production of lacquers and paints, synthetic fiber, magnetic tape), and *timber* productions, such as ethers (butyl acetate), aldehydes (formaldehyde), ketones (cyclohexane, etc.), aromatic hydrocarbons (xylene, toluene, etc.), *have an ecological value for marine hydrobionts, provided they reach the river mouths in less than 2–3 months (oxidizing period of pollutants)*;

(4) *The maximum concentrations of oil products* are contained in waste water of oil refining and petrochemical industry plants on oil extraction and treatment (up to 40,000 mg/L), production of bitumen, benzene, synthetic fat spirits, ethylene, propylene, polypropylene (1,000–2,500 mg/L), and in wastes of fish factories (up to 2,000 mg/L);

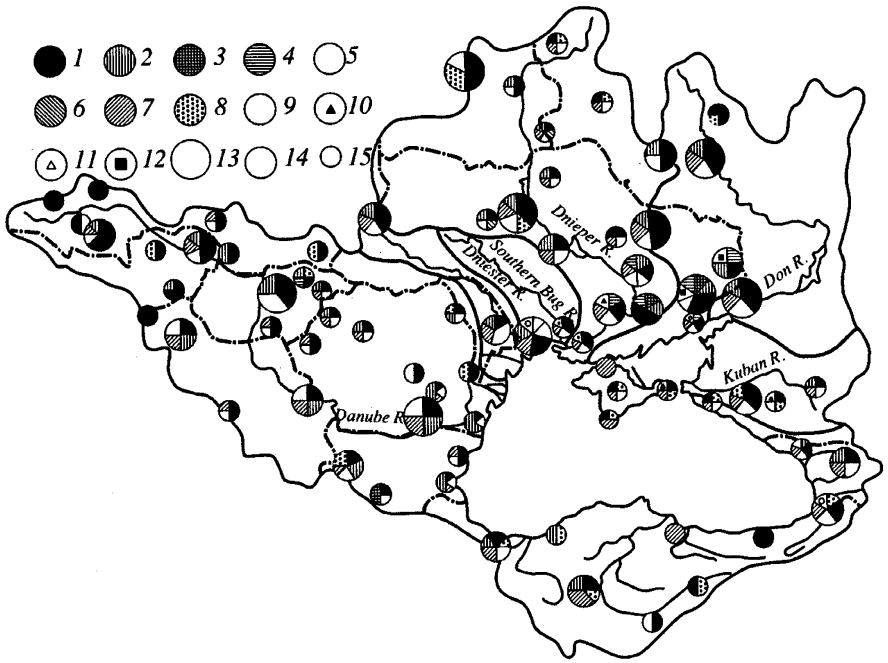


Fig. 1.24 Distribution of basic industries in the Black and Azov watershed basin: *1* metal fabricating industries, *2* ferrous industry, *3* chemical industry, *4* nonferrous metal industry, *5* consumer industry, *6* woodworking industry, *7* food industry, *8* construction materials, *9* resorts, *10* iron ore mining, *11* gas extraction, *12* coal mining. *Cities*: *13* >1 million people, *14* >500,000 people, *15* <500,000 people. *Borders*: *solid line* drainage basins, *dashed line* state

(5) *The maximum concentrations of detergents* (200–500 mg/L) are contained in wastes of hardware plants of *ferrous industry* (production of wire, electrodes, steel strap, steel net, fixing arrangements), wool-processing factories, and some other *customer industry* productions.

(6) *The maximum concentrations of phenols* are found in waste water of chemical-recovery plants of *ferrous metallurgy* (up to 200 mg/L), *chemical industry* plants producing synthetic fiber (up to 100 mg/L), lacquers and paints (up to 12,460 mg/L), and tanneries (up to 400 mg/L) of *customer industry*;

(7) *The maximum concentrations of copper* are registered in waste water of *nonferrous metallurgy* plants producing titan and copper under reverberatory smelting (200–350 mg/L), chemical fiber (to 300 mg/L) and ammonia (to 1,000 mg/L) manufactures of *chemical* industry, automobile and ball-bearing productions and instrument making (to 100 mg/L) of *machinery*, and also in wastes of all production types of *electronic* industry (up to 270 mg/L) and auto-repair plants (up to 400 mg/L);

(8) *The maximum concentrations of lead* are contained in waste water of *nonferrous metallurgy* plants on sulfur acid production (up to 2,860 mg/L) and *electrical industry* enterprises producing heat sources (100–300 mg/L);

(9) *The maximum concentrations of zinc* are contained in waste water of copper (220–850 mg/L) and sulfur acid (230 mg/L) production at *nonferrous metallurgy* plants; galvanic and pickling production (150 mg/L), instrument making (up to 100 mg/L) at *machinery* factories; and production of electric motors (200–400 mg/L) and condensers (more than 100 mg/L) at e*lectric industry* plants.

(10) *The maximum concentrations of chrome* are found in waste water of *chemical industry* plants producing pigments (100 mg/L); tanneries (190 mg/L) of *customer industry;electric industry* enterprises producing electric motors (60–160 mg/L), condensers (up to 600 mg/L), and semiconductor devices (100 mg/L); all production types of *electronic industry* (2,400 mg/L); and automobile, ball-bearing, and instrument making plants of *machinery* (up to 200 mg/L);

(11) *The main anthropogenic source of cadmium* for river and sea waters is associated with wastes of *electric industry* plants producing heat sources (100–300 mg/L), electric motors (up to 175 mg/L), and power semiconductors (130 mg/L);

(12) *The main anthropogenic source of arsenic for aquatic environment* is associated with *nonferrous metallurgy* plants producing copper and its compounds (140–1,000 mg/L), and lead and sulfur acid (up to 0.15 mg/L);

(13) *The main anthropogenic sources of manganese* for aquatic environment are *nonferrous metallurgy* plants producing titan (45 mg/L), and those of *petrochemical industry* producing synthetic fat acids (20 mg/L).

(14) Besides the indicated sources of specific heavy metals, various compounds of these trace elements can be contained also in waste water of lacquer-and-paint, machine-tool plants, and petrochemical industry enterprises (100–300 mg/L).

(15) Waste water of some production types of *chemical* (synthetic fiber plants) and *electric* (electric motor plants) industries, *machinery* (galvanic and pickling production, automobile, ball-bearing, instrument making plants), and of all *electronic industry* enterprises contain *cyanides* in concentrations from 10 to 400 mg/L.

In the presented list of ecologically hazardous industrial productions, the public utilities existing almost in all large cities of the watershed basin hold a specific place, being the powerful sources of detergents for natural waters

1.7.4 Integral Criteria of Ecological Importance of Watershed Territory for Marine Basin

For regionalization of watershed territory by level of its ecological importance for marine aquatory and visual presentation of this information several integral criteria can be used.

1.7.4.1 Index of Anthropogenic Load on Water Resources

(1) *The ratio of population density to mean annual river discharge from watershed basin* allows to estimate *the level of anthropogenic load on water resources of its territory*, i.e., to establish the population size per unit of freshwater drainage (Fig. 1.25). However, the combination of hydroclimatic and social factors determining the high values of this criterion, not always coincides with a character of distribution of industrial production. Many large industrial regions with dense population may be located in the zones of high mean annual drainage. In this case, the ratio value there is small, though the importance of these territories for the sea is beyond question. Thus, the areas with the maximum criterion values should be considered only as *zones of the higher probability of development of events dangerous to marine basin.*

(2) Untreated waste water of industrial plants located in the territory of marine watershed basins are, in case of their disposal in river systems, the powerful sources of conservative pollutants for coastal zones of the affected seas. To reconstruct the pattern of possible sources of the present pollution level of seawater, ground, and hydrobionts of the Black Sea by the specified contaminants we made (Fashchuk and Sapozhnikov 1999) the parallel analysis of their content in untreated waste water from various industrial sectors and

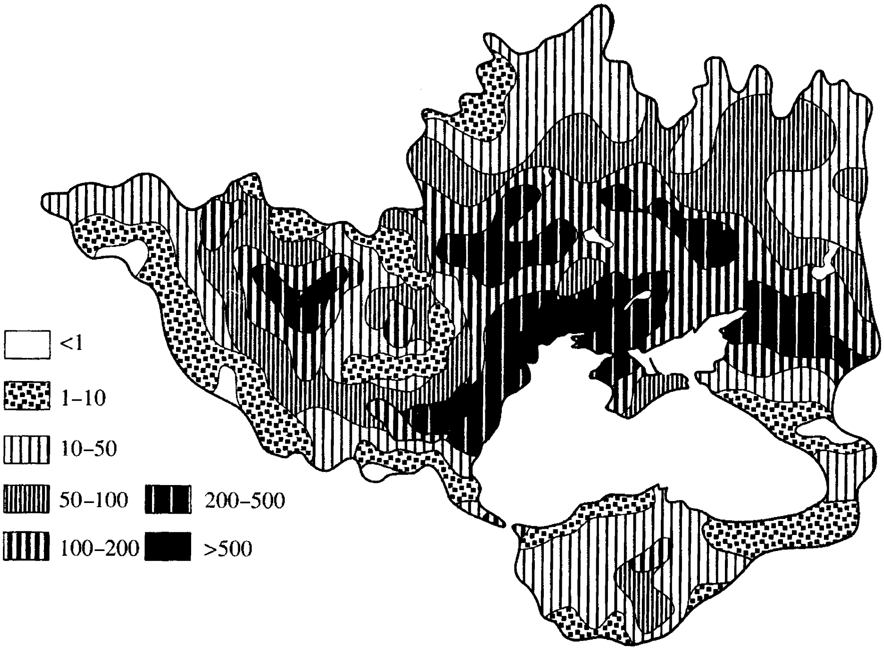


Fig. 1.25 Distribution of the index of anthropogenic load on water resources (people per $10^5 \times m^3$) of the Black and Azov Sea watershed

character of industrial production distribution by watershed basins of the Black and Azov Seas, with the use of reference encyclopedic data.

The results of this analysis allowed to rank the various production types by their ecological importance for marine aquatory and served as a basis for regionalization of watershed territory by degree of potential ecological danger to marine basin (as possible source of pollution by industrial wastes).

Such analysis requires introduction of the correction coefficients counting: *ecological weight of toxicant, distance of toxic manufacture from the sea, disposal volume and degree of its waste water treatment, transformation rate of appropriate pollutant in aquatic environment, flow velocity of the river, in which waste water are discharged, or volume of freshwater runoff from the drainage basin territory, in which the manufacture is located, etc.*

1.7.4.2 Index of Potential Ecological Danger of Industrial Production in the Watershed Basin to Marine Aquatory (PED)

As the quantitative criterion of potential ecological danger (PED) of industrial production in the cities located on coast and banks of main rivers to marine aquatories, the sum of ratios of the toxicant concentration in waste water to its

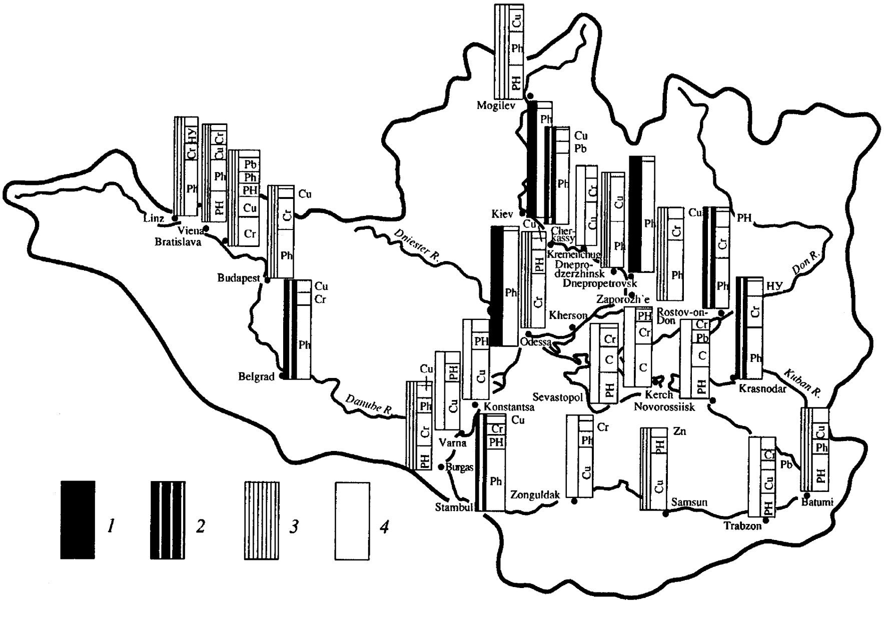


Fig. 1.26 Distribution and structure of the index of potential ecological danger (PED) of industrial waste water of the Black Sea watershed basin to its aquatory. *PH* petroleum hydrocarbons; *Ph* phenols; the white area—other pollutants Logarithmic scale: *1–4* >1; 0.5 > 1; 0.1 > 0.5; <0.1 millions MAC, respectively

MAC in marine aquatic environment, i.e., *the total amount of the maximum exceedances of MAC by all investigated persistent toxicants containing in industrial waste water of appropriate city*, is taken.

After the corresponding calculations, the values of the PED index for each of the 30 analyzed cities were plotted on the map of watershed basins of the Black and Azov Seas in form of diagrams. The relative weight of each pollution component was calculated from a simple proportion and was also plotted on the diagram. This allowed to present visually the spatial distribution of the PED index and its structure by the territory of investigated watershed basins (Fig. 1.26).

1.8 Conclusions

Thus, for solving the problems of marine ecology, in parallel with the traditional methods of data generalization, it is proposed to analyze them on the basis of the information model representing a complex of geographic and ecological aspects of the “sea-watershed” system study by various sciences. The logic scheme of research includes a number of operations: selection, “condensing”, analysis and visual presentation of information, ranking of processes by their ecological importance, identification and mapping of adverse consequences for marine life. For this purpose the algorithms of ecological indicators and methods of marine ecological mapping were developed. This allowed to “condense” numerous digital and cartographic materials to analytical tables and diagrams, marine diagnostic ecological maps and general schematic maps.

Realization of the proposed methodological principles of geographic and ecological approach allows:

- *To create theoretical and information base* of advanced development and calculations of integral criteria for assessment of marine ecosystem state in response to economic activity, and for realization of mathematical models of marine ecosystems;
- *To systematize the ecological information* for any basin of the World ocean, using the structure of information base, methodological principles of construction of its geographic and ecological model—“portrait”;
- *To estimate operatively the possible causes* of development of crisis situations in the sea, reduce a zone of their operative search, develop the scientifically based nature protection measures on the basis of the parallel analysis of maps and “portrait” description;
- *To estimate operatively the possible consequences* of catastrophic impact on marine ecosystem (volley of pollutants with river runoff or waste water discharge of coastal enterprises, tanker wrecks or accidents with oil pipelines) for populations of commercial hydrobionts, orientate the industry at planning of marine biological resources development;

- *To develop the forecast* of possible ecological changes in coastal areas of the sea in case of disturbance of waste water treatment regime, based on the analysis of map of potential ecological danger of industrial production in the watershed territory to marine aquatories;

The information geographic and ecological model of the Black Sea based on these principles includes (Fashchuk 1997):

- Retrospective maps of paleogeographic reconstructions of ancient basins;
- Integral schematic map of life distribution in the basin;
- Integral schematic map of main natural factors forming environmental conditions in the basin;
- Integral schematic distributional map of types of anthropogenic impact on the Black Sea ecosystem and its adverse consequences;
- Map of anthropogenic loads on water resources of the Black and Azov Sea watershed basins;
- Map of the index of potential ecological danger of coastal industrial plants to marine aquatories and its structure;

The suggested model has allowed to formalize the cause-and-effect ecological relationships existing in the “Black Sea-watershed basin” geosystem due to the impact of natural and anthropogenic factors, for development of geographic and ecological forecasting, namely:

- To regionalize aquatory by tolerance of commercial organisms to external impacts, having identified the life concentration centers at different stages of their development;
- To estimate the optimum habitat conditions for various hydrobiont species and priority natural factors of their formation;
- To identify the marine areas with anomalous pollutant content in water, ground, and hydrobionts and to define scales and structure of these anomalies;
- To estimate the level and structure of anthropogenic pollution load on various shelf areas and the Dnieper and Danube rivers;
- To regionalize the watershed basin by index of anthropogenic load on its water resources and to identify the areas most dangerous to the sea by combination of social (population density) and climatic (river discharge) factors;
- To regionalize the coast of the sea and its main rivers by value and structure of the index of potential ecological danger of industrial production, having defined the cities with the high content of persistent toxicants in waste water of their industrial plants.

The parallel analysis of a set of maps, diagrams and model descriptions allows to reduce the time of estimation of the possible causes of development of crisis situations in the sea or to narrow their search zone. Father, it is possible to solve the inverse problem of prediction of the possible changes in environmental conditions and hydrobiont state in case of development of natural anomalies or under the intensification of economic activity on marine aquatory and watershed, in the same manner.

Taking into account a huge volume and diversity of data analyzed during the development of geographic and ecological model of the Black Sea, it is difficult to exclude the probability of missing of some ecologically significant results under the analysis. In this context, the possibility of further enrichment of the suggested model with getting a new knowledge in various fields of marine science, or under the analysis of geographic and ecological aspects of already available information for its further use as a basis at realization of mathematical models, is obvious.

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Chapter 2
Mathematical Modeling of Marine Ecosystems: Geographic and Ecological Aspects

Owing to efforts of the classics of modern natural science, during the history of its development the qualitative model of the outside world was formed. So, V.I. Vernadsky laid the basis for the doctrine about living matter and marine geochemistry (Vernadsky 1923, 1934), A.P. Vinogradov started to study a chemical composition of microorganisms (Vinogradov 1935), N.M. Knipovich was the pioneer of fishery research of the seas and brackish waters (Knipovich 1938), S.V. Bruevich developed the analytical methods of marine hydrochemical investigations and formulated the fundamentals of hydrochemistry, biohydrochemistry, and chemical dynamics of the seas (Bruevich 1933, 1978), L.A. Zenkevich studied fauna and bioproductivity of sea waters (Zenkevich 1947), A.B. Skopintsev started the investigations of nutrients and organic matter in water reservoirs and streams (Skopintsev 1950), G.G. Vinberg considered the problems of biological productivity formation in the seas (Vinberg 1960).

These works have served as the methodological and theoretical basis of regular investigations on the ecological state of marine ecosystems, hydrochemical features of formation of fishery resources and bioproductivity of natural waters; regularities of development of chemical and biological processes of organic matter transformation and disintegration; mechanisms of nutrient substrate regeneration in connection with study of the cycle of matter conditions in biosphere (Leonov 1999) which started in the second half of the twentieth century worldwide, and also methods of systematization and analysis of the obtained information (Fashchuk 1997; Fashchuk et al. 1997).

2.1 Types of Mathematical Models of Marine Ecosystems

According to the known mathematician, academician I.M. Yaglom: "*The maturity level of any discipline is determined to a great extent by degree of the use of*

D. Y. Fashchuk, *Marine Ecological Geography*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-17444-5_2,

Photo 2.1 Today mathematical models of marine ecosystems, together with field observations at sea, have become a basis of scientific understanding of ocean nature. (Atlantic Ocean by J. Gangnus)

mathematical apparatus in it, content-richness of "mathematical models" inherent in the discipline and associated deductive conclusions…" (Photo 2.1).

By the second half of the twentieth century marine ecology "has maturated" as a science so much that mathematical modeling of marine ecosystem state became an independent scientific direction in natural science. Within its framework the World Ocean is considered as a complex dynamic system of physical, chemical, biological, geological and other processes. The development of computer aids and apparatus of applied mathematics resulted in the intensive building of mathematical models of marine ecosystems which allowed to systematize the obtained knowledge in various fields of marine science for the purpose of forecasting and management of marine basin state.

There are several types of mathematical models of marine ecosystems. *Depending on the purposes of modeling*, they can be divided into *simulation models* confined to specific basins or regions and developed for specific purposes, and *qualitative*, theoretical models used for elucidation of the general regularities of process development and their analysis. In simulation models scientists aim to consider the maximum number of variables, while in qualitative models only the most important characteristics are counted. Therefore, the main problem for them is associated with a choice of priority variables (Smith 1976).

By method of realization, the models are divided into *deterministic* models which use functional dependences for description of the relationships among variables, and *stochastic* models based on statistical relationships. The former are used more often because they permit infinite set of components and do not consider random fluctuations of environmental parameters. They are convenient in terms of interpretation of the results (Aizatulin and Lebedev 1977). There are also *stochastic and deterministic* models in which at the first stage the solution is sought deterministically, and then, by means of Monte-Carlo technique the variability of various parameters is modeled and response of the solution to this variability is studied.

By method of representation of the phenomenon spatial structure models are separated into *point* (parameters are concentrated in one point), *reservoir* (distribution of parameters is limited by borders–box walls), and *continuous* (real spatial distribution of parameters is taken) models.

In point model the characteristics are integrated by whole volume of the considered area. In reservoir model each element of spatial area described by the space-averaged parameters (river section, ocean layer), is called *reservoir* (box), and in state space (food link, suspension, dissolved matter) it is called *block*. Transfer of properties from one reservoir to another is conventionally called *flux*, and that from one block to another—*transition* (Niul 1978).

In reservoir models the considered volume is divided into separate reservoirs, for each of which only the reservoir—averaged concentration of substance is considered and the point model is constructed. It allows to account with some degree of certainty the spatial heterogeneity and to define any structural objects. The main advantage of reservoir models is simplicity of their realization, though in the real nature it is difficult to identify the representative system of reservoirs and to attribute the appropriate parameter values to them. Moreover, these models are sensitive to small fluctuations of parameters (Kagan and Ryabchenko 1978).

In continuous models there is no spatial averaging, and at every instant the solution is represented by the smooth curve (or field) of parameter distribution. These models are usually reduced to solution of the simplified thermodynamics differential system (two motion equations, static equation, equation of continuity of incompressible fluid, heat and salt-transfer equation, equation of state), and equations for the studied characteristics similar to equations of heat and salt balance.

When implementing the problems of modeling of chemical and biological characteristics, the solution of system of thermohydrodynamics equations (simulated fields of current velocity, temperature, salinity) is substituted in the parameter—transfer equations. Thus, the chance to study their transformation caused by chemical, biological, and biochemical processes, together with their mass transfer, appears (Aizatulin 1974).

The choice of a particular model type depends on the problem facing the researcher. Thereupon, sometimes the preference is given not to complex but primitive models, because of their ability to answer the specific questions.

2.2 Objectives of Mathematical Modeling in Marine Ecology

The development of methods of oceanological investigations including all fields of marine science (physics, chemistry, biology, geology) and interdisciplinary sciences—hydrobiology, biophysics, biochemistry, biogeo—and hydrochemistry, has determined the accumulation of the huge factual material reflecting various aspects of marine ecosystem functioning during the 1930s–1960s (Photo 2.2). As a result, the necessity to systematize and generalize the obtained data, formalize the existing ideas in the form of mathematical models to forecast the dynamics of natural water properties by main chemical and biological parameters, has appeared.

Photo 2.2 Changes in character of water consumption occurred in the 1940s–1960s, growth of waste water discharge volumes put ecologists before necessity to study the prospects of marin and lake ecosystems variability with use of mathematical models. (Atlantic Ocean by Yu.Maslyaev—top; Balaton Lake by [www.hungarystartshere.com]—bottom))

At the first stages of such systematization in the 1920s–1930s, the integral indicators of matter transformation in natural waters and water basin state were studied, with use of the models reproducing (*the dissolved oxygen regime, depending on content of labile organic matter* (*OM*) *in units of chemical or biochemical oxygen demand*) (COD and BOD, respectively). Moreover, the attention was given to *the trophic interpopulation relationships of organisms* (e.g., “predator–prey”).

Among the chemical and biological processes developing in marine environment, the special attention under modeling is given to the mechanisms determining transformation and biogeochemical cyclicity of elements entering into the composition of living matter (*C, N, P, S, Si*). Thus, at the first stages of modeling the attention was drawn to *rates of decrease in concentration of chemicals, utilization and consecutive transformations of substrata by organism community, and rates and mechanism of transformation of chemicals*. As a result, the following important practical problems have been solved:

(1) The quantitative information on spatiotemporal changes in chemical and biological characteristics of marine ecosystem, depending on intensity of

impact of environmental factors (temperature, light conditions, transparency, water regime, nutrient load) on it, was obtained.

(2) Pollution assimilative capacity of marine ecosystem was assessed, and recommendations on creation of the most effective conditions for this process were developed.
(3) The matter balance in natural waters with account of exchange fluxes at the water-atmosphere and water-bottom interfaces, supply of matter with waters of tributaries and atmospheric precipitation, and losses of matter at their export by water masses from the basin, was drawn up.
(4) A role of natural and anthropogenic processes in nutrient cycle of marine ecosystems was established. On this basis the measures on water resources conservation were developed; natural water reserves and potential of their quality were estimated; methods of pollution control and mechanisms of water purification were defined.
(5) The nutrient stock in natural waters and its spatial and temporal variability influenced by processes of their consumption by planktonic organisms and regeneration under the OM destruction was estimated. The bases of primary production in basins and their biological productivity at the higher trophic levels were studied.
(6) The behaviour and distribution of populations, communities of organisms in marine environment were studied; the features of vertical heterogeneity and horizontal patchiness of hydrobionts distribution were reproduced (Vinberg and Anisimov 1966); the role of predators in regulation of photosynthetic activity of phytoplankton was defined (Vinberg and Anisimov 1969).
(7) The vertical structure of microorganism communities—biomass of various phyto- and zooplankton groups, detritus, in tropical zone of the ocean (Vinogradov et al. 1972), in pelagial of the Sea of Japan (Menshutkin et al. 1974) an Peruvian upwelling (Fleishman and Krapivin 1974) was studied.
(8) The reasons of intensification (outbursts) of biological communities development (Petrovsky et al. 1998), invasion of new species in ecosystems (Keondzhyan et al. 1990), and blooming of certain alga groups were investigated (Photo 2.3).

Now the relevant objectives of mathematical modeling of biogeochemical processes in marine ecosystems are: study of chemical and biological process rates, cycle of matter in natural waters, conditions of biological productivity formation in basins, estimation of balance of organogenic element compounds in aquatic environment, and the complex research on processes of chemical exchange at interfaces “water–atmosphere,” “water–bottom” and chemical and biological transformation of matter in aquatic environment and bottom sediments.

When studying a complex of hydrodynamic processes developing in marine environment, the great attention under mathematical modeling of marine ecosystems state is given to problems of horizontal and vertical transfer of pollutants, establishment of conditions of formation and disintegration of marine organism (phyto- and zooplankton, pelagic and bottom commercial objects) concentrations, redistribution of life by depth (Menshutkin and Finenko 1975).

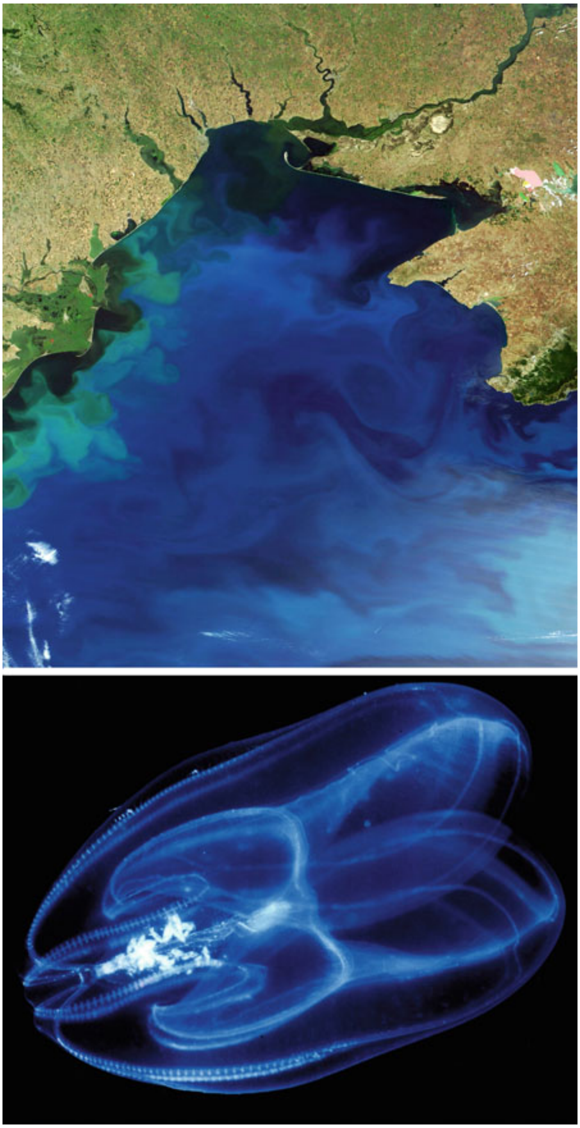

Photo 2.3 Development of “red tides”, outbursts of phytoplankton blooming, in marine basins ((*top*)—Black Sea NW shelf, by [veimages.gsfc.nasa.gov]) and populations of new invading species ((*bottom*)—Mnemiopsis Leidyi, by [www.people.bu.edu]) is one of the major spheres of “interests” of marine ecosystems modeling today

2.3 Models of Biochemical Processes in Marine Ecosystems

According to existent ideas of character of ecological data generalization, there is a predominance of mathematical analysis of information at its first stage, modeling at the second stage, and development of the mathematical theory at the third stage. By the 1980s the level of mathematization of marine ecological science has corresponded to the first stage, though the first tenuous steps within the second stage have been made yet in the beginning of the twentieth century, when Streeter–Phelps model of oxygen regime of rivers and Lotka–Volterra model of predator–prey interactions were developed, and in the world there were about 150 mathematical models of water basins and watercourses of various complexity (Aizatulin and Shamardina 1980).

More than hundred from this number have been developed for lakes and reservoirs, with a third of them created by native authors. The ecosystems of Great Lakes, Bratsk, Ivankovo, Rybinsk, Mozhaisk, Zeya, Dnieper and other reservoirs were modeled.

Thus, together with problems of basin eutrophication, estimation of energy fluxes and productivity, the questions on influence of intermittent land flooding on ecosystem, mass blooming of reservoirs were solved. The majority of these models are the point correlation—regression and point or two-reservoir models of primary production and budget of phosphorus as limiting factor and factor of eutrophication of water systems Simulation models comprised only 10% in the total number of mathematical developments and numerical experiments.

By 1980 a large number of the developed models were used for ecosystem study of continental sources, rivers, brooks, and also intermittent water bodies and ponds as the simplest modeling objects. There were only a few models which tried to describe state of the whole marine ecosystem or its specific areas.

By the beginning of the twenty first century many simulation models capable of analytically and numerically investigating changes in the major chemical and biological characteristics, occurring in aquatic ecosystems, have been already developed in the world. Their detailed review is presented in numerous literary sources (Vavilin 1986; Dombrovsky et al. 1990; Tskhai 1995; Leonov 1999), etc.

Nevertheless, the majority of models concerning the problems of transformation of matter in marine environment under biochemical processes are the point or reservoir models. In spatial models these problems receive less attention, and emphasis is made on the analysis of spatiotemporal variability of hydrochemical and biological components of aquatic ecosystems (Fashchuk et al. 2005).

2.3.1 Formalization of Biochemical Processes in Mathematical Models

Biogeochemistry studies chemical biogenic (organogenic) elements and their mineral compounds. Among them the main elements are those composing living organisms: carbon, oxygen, phosphorus, nitrogen, sulfur, silicon and some other (Ivanenkov 1979). Moreover, micronutrient elements, among which iron and manganese are the most important, include almost all elements found in the ocean. Vernadsky (1934) defined organogenic elements as cyclic elements undergoing the reversible processes. Their cycles are reversible only in body of atoms, and part of atoms comes out of the circulation (Vernadsky 1934).

The spatial and temporal variability of nutrients participating in reversible cycle, determines two groups of processes in the ocean. The first group includes chemical and biological redox and absorbtion—desorption processes changing concentrations of properties in specific volume of water. The hydrophysical processes of advection and turbulence belong to the second group, responsible for transfer of chemical elements conditionally considered as passive impurity. For suspended forms of nutrients the processes of their passive settlement (sedimentation) are also of great importance. All these processes determine the dynamics of chemical substances in marine ecosystem. Moreover, the exchange processes at the atmosphere—water and ground—water interfaces are also very important in mathematical ecological modeling (Bruevich 1978).

Unlike distribution models of hydrophysical parameters of marine ecosystem state, based on solution of standard differential equation system, in biochemical models there is no such system of equations. There are only accepted methods of parametrization of modeled processes. Thus, the ratios between space and time scales of hydrophysical processes within which they are capable of affecting the formation of spatial distribution of hydrochemical and biological parameters, are enormously important. According to Monin (1982), the spatial heterogeneities are characterized by typical time scales of processes generating them (Table 2.1): *small scale* (fractions of millimeter—tens of meters)–from 10^{-3} s to tens of hours;

- *mesoscale* (hundreds of meters—kilometers)–from hours to days;
- *synoptic* (tens and first hundreds of kilometers)–from days to months;
- *global* (thousands and tens of thousands kilometers)–from years to hundreds of years.

Table 2.1 Processes affecting distribution and variability of chemical substances in the ocean (Monin 1982)

Process	Scale (sec)	Lifetime	Source
Gaseous interchange between ocean and atmosphere	10^1	Tens of seconds	Emerson (1995)
Hydrolysis of gases and processes in carbonate system	10^1	Tens of seconds	Emerson (1995)
Physiological rhythms of marine organisms	10^{5-6}	Hours–months	Rudyakov (1986)
Advective and turbulent transfer (surface waters)	10^{6-7}	Days–year	Monin et al. (1974)
Chemical and biological	10^{6-7}	Days–year	Monin et al. (1974)
Anthropogenic CO_2	10^9	30–40 years	Gruber et al. (1996
Oxidation of persistent aquatic humus (suspended organic matter)	10^{11}	2,000 years	Skopintsev et al. (1979)
Advective and turbulent transfer (deep waters)	10^{11}	1,000 years	Monin et al. (1974)
Sedimentation	$>10^{12}$	>10,000 years	Monin et al. (1974)

It is obvious that at any time scale several processes actively affect the formation of hydrochemical fields that should be taken into account, when creating the mathematical model. In the upper ocean layer where chemical and biological processes are the most important, every process is corresponded by certain characteristic time and characteristic values of component concentrations. With depth this regularity is broken. In this case, the concentrations of living organisms and organic matter decrease exponentially, while concentrations of nutrients (e.g., phosphates) grow. With that, the characteristic scales of change in concentrations of dissolved inorganic forms of nutrients and their suspended organic forms, including those in living organisms, differ by more than 4 orders of magnitude. Thus, the method of parametrization of chemical and biological processes should be connected with scales of variability in concentrations of chemical forms in the selected modeling object and spatiotemporal scale of the solved problem.

The chemical and biological processes imply a complex of processes, including the synthesis of organic matter from inorganic compounds, its transfer in trophic chain, elimination of organic and inorganic substances from living and dead organisms, autolysis of suspended material, and organic matter degradation. The process of OM synthesis and degradation proceeds under the classical Redfield stoichiometry (Redfield 1934) with account of interchange of matter among various organisms within an ecosystem.

When modeling (*nutrient uptake under the synthesis of organic matter photosynthesis*), the following statements are taken into consideration (Sergeev 1979):

- Specific rate of photosynthesis is directly proportional to phytoplankton biomass and rate of nutrient uptake;
- Average sizes of phytoplankton cells and their chemical composition are identical and constant; autotrophic growth ceases at zero values of sunlight and nutrient concentrations.

With that, the complex ambiguous dependence of photosynthetic intensity on intensity and duration of sunlight, nutrient concentrations in the environment and cell, water temperature and salinity, size and species of alga is considered (Photo 2.4).

When describing photosynthesis, the majority of ecosystem models lean on the concept of limiting factor governing the rate of this process. According to Liebig's Law formulated in 1840, the rate of photosynthesis is limited by that chemical element, for which ratio of its concentrations in the environment and marine organisms, is minimal. In 1905 Blackman expanded this law with the concept of limiting factor, and in 1911 Shalford formulated the more general principle of l tolerance, lying in the fact that tolerance of organism (species) was determined by both maximum and minimum of ecological factor range (Aizatulin and Shamardina 1980; Reimers 1980). When modeling marine ecosystems, one of nutrients (nitrogen, phosphorus, or more rarely silicon) is usually used as limiting factor. However unlike Liebig's Law, the concentration of limiting factor only in water but not in organisms figures in these models.

Photo 2.4 Experimental study of mysteries of photosynthesis performed by fluorocarbons (*on photo*) of phytoplankton cells seems quite difficult without mathematical modeling

When modeling *the elimination of nutrient compounds from autotrophic organisms*, their entry into marine environment in the process of breathing (inorganic compounds), exudation (loss of organic matter as a result of vital activity of marine algae which can reach 40% of net daily production), and at die-away is taken into account (Parsons et al. 1982).

When modeling *the transformation of nutrient compounds by heterotrophic organisms*, their uptake by autotrophs (phytoplankton) and formation of dead organic matter (detritus) by zooplankton (Menshutkin and Finenko 1975; Aizatulin and Leonov 1975, 1977; Leonov 1980; Fasham et al. 1990), elimination of these compounds in the process of breathing, metabolism (Sergeev 1979) and die-away of zooplankton in the form of dissolved inorganic and suspended organic matter (Shushkina 1977; Sazhin 1982; Rudyakov et al. 1984), and also at grazing of some heterotrophic organisms by others is considered.

2.3.2 Point Models

In the 1960s K. Wyrtki modeled the vertical distribution of hydrochemical characteristics in marine ecosystems. In his one-dimensional model the formation of layer of oxygen minimum and phosphate maximum in intermediate waters of the ocean was investigated. The model considered biological oxygen demand and vertical turbulent exchange that allowed obtaining the good agreement with picture observed in the ocean and running numerical experiments on change in the studied characteristics under the influence of model parameters (Wyrtki 1962).

In that time Watt and Hayes, based on the analysis of samples taken in the area of Halifax (Canada), have proposed the model considering three forms of phosphorus: dissolved inorganic (DIP), dissolved organic (DOP), and particulate (PP). The fitted coefficients reflected adequately the dynamics of phosphate formation in the sea even during the expedition (Watt and Hayes 1963).

In the 1970s this model has been improved by division of particulate phosphorus into 3 constituents (bacteria, zooplankton and detritus). For description of phosphorus transformation with account of bacteria and zooplankton the first–order chemical equations, equations in the form of the Michaelis–Menten scheme, and a number of other schemes of consecutive transformation of chemical forms of phosphorus were used (Aizatulin and Leonov 1975; Leonov and Aizatulin 1977).

The point non-stationary Steel's model reflects the common features of seasonal dynamics of phosphates and phytoplankton concentrations in the photic layer of the North Sea. The model considers the phosphate amount and phytoplankton biomass. For description of their dynamics in open system the seasonal variability of sunlight, mixing, sedimentation, concentration of zooplankton consuming phytoplankton as food were taken into account (Steel 1959, 1962; Steel and Frost 1977). The similar problem for the Baltic Sea was solved in more detailed model considering the seasonal transformation of nitrogen compounds. In this model, along with nitrates, nitrites, ammonium and dissolved organic nitrogen, phyto- and zooplankton were introduced also (Savchuk 1977).

The point simulation Hornberger-Spear model is devoted to study of estuary eutrophication impact on growth of benthic algae. In the model the transformation of phosphorus forms in estuary waters, sediments, phytoplankton, and benthic algae is considered. It uses the Michaelis–Menten dependences and first-order equations and accounts the influence of sunlight, temperature and phosphorus intake from external sources (with river and rain waters). The seasonal variability of P forms, with the estimation of contribution of various processes, is calculated (Hornberger and Spear 1980).

In 1990 the Fasham-Ducklow-McKelvie model describing seasonal dynamics of nitrogen compounds in the upper mixed ocean layer has appeared. In this model the transformation of nitrates, ammonium, the labile dissolved organic nitrogen and detritus with the participation of phyto-, zooplankton and bacteria was considered. The model became the reference standard for modeling of both the large-scale features of global biogeochemical cycles and other, faster, processes in aquatic environment (Fasham et al. 1990).

The seasonal variability of vertical hydrochemical structure was investigated with use of the Flasham's model by the example of real observational data (Fasham et al. 1993; Kawamiya et al. 1995). Further, Savchuk and Wulff (1996) studied the vertical distribution of various forms of phosphorus (phosphates, detritus), nitrogen (nitrates, ammonium, detritus), oxygen and biological characteristics (phyto- and zooplankton), with estimation of a role of various factors in formation of vertical hydrochemical structure of deep Baltic Sea, using their own model (Savchuk and Wulff 1996).

2.3.3 Box Models

In the set of models of this type initiated by Swedish scientists, the components of mass transfer are estimated by nutrient deficit in box, based on investigations of the World Ocean circulation (Bolin et al. 1983).

The Postma's box model considers the phosphorus balance in the World Ocean divided into 9 homogeneous boxes with account of the processes of consumption, regeneration, sedimentation, and exchange. Using the same model, Sarmiento et al. (1990) investigated the influence of Atlantic subtropical gyre on transport of radioactive tracers, nitrates, and oxygen that allowed them estimating the characteristics of new production by nitrates and biological oxygen demand (Sarmiento et al. 1990).

The box model was successfully applied to studying the Lake Balaton ecosystem in Hungary (Leonov 1986), dynamics of phosphorus forms, functioning conditions of some aquatic ecosystems of Finland (Varis et al. 1986; Leonov and Niemi 1989; Leonov 1989a). One of the versions of this model involving forms of nitrogen and dissolved organic matter, was used for research of the Lake Ladoga ecosystem (Leonov et al. 1991). The later model version allows estimating the transformation of main compounds of organogenic elements (carbon, nitrogen, phosphorus, oxygen) (Leonov et al. 1994). The modern model version accounts the characteristics of pollution (oil products, pesticides, heavy metals, phenols), phytoplankton production, and concentration of substances in bottom sediments (Leonov 2000). Several complex developments were used for study of the Okhotsk (Leonov and Sapozhnikov 1997; Pishchalnik and Leonov 2003) and Caspian (Leonov and Sapozhnikov 2000) Sea ecosystems. When modeling the Sea of Okhotsk, the cycles of nitrogen, phosphorus, and silicon were studied in parallel. In total, 18 blocks were considered, six of which included living organisms. The sea was divided into 8 boxes ("aquatories"), with mass transfer among them. The similar calculations were made for ecosystem of Aniva Bay on the Sakhalin shelf (Leonov and Pishchalnik 2005) and northwestern shelf of the Black Sea (Leonov and Fashchuk 2006).

It should be noted that a great contribution to studying biohydrochemistry of natural waters, developing the methods of mathematical modeling of simultaneous biological and chemical transformation of matter in marine ecosystems was made by T.A. Aizatulin. For the first time in native practice he has directed attention to formalization of cycles and mechanisms of transformation of nutrient compounds under the analysis of dynamics of hydrobiont biomass and nutrient concentrations in the sea. He proposed the chemical and kinetic apparatus describing the regeneration of mineral components of nutrients (Aizatulin 1967) and processes of transformation of organic and inorganic metabolites as an important link of the whole chemical - ecological system (Aizatulin 1974).

The models based on such chemical and kinetic approach were intended first for study of dynamics of dissolved oxygen concentration and oxidation of organic matter (Aizatulin and Leonov 1975) and joint cycles of sulfur and oxygen (Aizatulin and Leonov 1990), nitrogen and oxygen, phosphorus and oxygen, carbon, phosphorus and oxygen (Leonov and Aizatulin 1977), nitrogen, phosphorus and oxygen (Leonov 1989b) in closed systems. In later developments the joint cycles of nutrients in their various combinations in marine environment were modeled, using from several to several tens of equations describing the dynamics of biological community, concentrations of various nutrient forms, and biomass of organisms transforming matter (Vinogradov et al. 1989; Leonov and Aizatulin 1995; Leonov and Sapozhnikov 1997; Yakushev 1998).

2.3.4 Continuous Models

In the middle of the twentieth century the large-scale meridional distribution of phosphates in the Atlantic ocean was investigated with use of the continuous model. With that, the currents were calculated by dynamic method on a $5 \times 5^\circ$ grid, in each point the difference between consumption and elimination of phosphates was compensated by their transfer due to physical processes (Riley 1951). It was the first attempt to investigate the distribution of hydrochemical characteristics in the ocean by means of mathematical modeling.

The oxygen distribution at meridional section of Atlantic ocean was studied by means of continuous two-dimensional model, in which the surface oxygen distribution and its biological consumption in water column were prescribed. The accepted scheme of circulation reflected two gyres in the Southern Hemisphere and one gyre—in the Northern Hemisphere (Bubnov and Krivilevich 1973).

To analyze oxygen regime in waters of the World ocean the integral two-dimensional scheme of the World Ocean circulation calculated on a $5 \times 5^\circ$ grid, was used. With that, the oxygen flux through the ocean surface, spatial variability of production, and oxygen consumption were considered. In this case, for construction of hydrochemical model the “prepared” scheme of water circulation was used (Ryabchenko 1977).

In last decade such approach has become dominating. In coupled models the hydrophysical representation of specific object is combined with model of biogeochemical transformation nutrients. For the Black Sea the scheme of biogeochemical sources “phytoplankton–zooplankton–dissolved organic matter–nitrates–ammonium” is used (Gregoir et al. 1997), and elements of global transport of organic matter are studied with use of the three-dimensional circulation model and simplified model of biogeochemical transformation of phosphorus (Najjar et al. 1992).

The complex simulation model of the Sea of Azov considered the problems of economic activity impact on water resources of the basin (Gorstko 1976; Bronfman 1976; Gorstko et al. 1982) (Photo 2.5). Along with biological components of various trophic levels, the model takes into consideration the concentration of nutrients as an indicator of eutrophication level of marine ecosystem. The cycle of phosphorus, nitrogen and silicon compounds with account of the processes of

Photo 2.5 In the 1970s Rostov scientists developed the first continuous complex model of the Azov Sea ecosystem (Cape Kazantip—Azov Sea in summer and winter – photo by V. Kaminsky)

their transfer, disintegration, consumption, abrasion of coast and other factors is described. The modern development of the Rostov modeling school is reflected in monograph (Matishov 2001).

2.3.5 Hydroecological Model of Organogenic Element Transformation

After the analysis of existing experience in study of marine basin nature by mathematical methods (Fashchuk et al. 2005), the simulation box hydroecological model of organogenic element transformation in marine environment, developed in the late twentieth century by A.V.Leonov, was chosen for solving the problems of marine ecological geography. To study the regime of oil product transformation in marine ecosystem, the chosen model, instead of *abundance and biomass* of oil oxidizing bacteria, considers *their biochemical activity*, i.e. ability to perform the cycle of processes including consumption of food substrates, elimination of microbial products, formation of detritus. The model describes the interrelated biogeochemical cycles of such elements as N and P, and also includes the description of transformation rates of Si, dissolved organic C (DOC) and oxygen O_2 in a two-layer aquatic ecosystem. Thus, the dynamics of concentrations of DOC, O_2, N–, P–, and Si-containing substances is estimated under their biotransformation and development of exchange processes at the water–air and water–bottom interfaces. The model accounts the following P, N and Si compounds: detritus P, dissolved inorganic P, organic P, organic N, ammonium N (NH4), nitrite N (NO_2), *nitrate* N (NO_3), *urea* N *and free nitrogen* (N_2), *inorganic* Si, *organic* Si, *detritus* Si.

The biotransformation of organogenic element compounds reproduced by the model is performed by community of microorganisms: *heterotrophic bacteria* (*B*) *consume organic compounds and in the process of metabolism form a pool of inorganic substances; phytoplankton* (*F1, F2, and F3*) *utilizes inorganic substances and forms a reserve of organic substances in aquatic environment; zooplanktonic organisms* (*Z1 and Z2*) *regulate the dynamics of community organisms and through their own activity affect the development of production—destruction processes.*

Actually, the model reproduces transient processes and describes response of aquatic ecosystem to changes in environmental conditions or to change in at least one of factors considered in the model (water regime, temperature, sunlight, nutrient load). It contains 226 equations describing:

- change in concentrations of components under study;
- specific rates of organogenic substance utilization by heterotrophic bacteria, phyto- and zooplankton;
- functions and correction coefficients on temperature and sunlight intensity for constants of substrate utilization rates by hydrobionts;
- specific rates of metabolic eliminations and elimination activity of organisms;
- specific rates of organism die-away;
- total rates of change in microorganism biomass due to interaction of chemical and biological components of community under consideration;
- total rates of change in nutrient concentrations in aquatic environment and sediments;
- rates of substance supply from external sources (atmospheric precipitation, distributed sources).

When estimating the rates of change in concentrations of organogenic substances due to horizontal and vertical transport, the following is considered:

- entry of these substances into marine aquatories with tributary waters;
- replenishment of substance reserve due to vertical exchange with underlying layer;
- transport of substances from adjacent aquatories within the marine ecosystem and their loss under an export outside the ecosystem by water flow.

The block of biochemical transformation of oil products by oil-oxidizing bacteria includes 10 equations describing:

- change in concentrations of oil products and biomass of oil oxidizing bacteria;
- total and separate utilization of substrates (oil products and DOC) by oil oxidizing bacteria;
- activity function of oil oxidizing bacteria, depending on temperature;
- specific rates of elimination of metabolic products and die-away of oxidizing bacterium biomass.

Thus, the model describes the intraannual dynamics of chemical and biological indicators of aquatic environment state, instantaneous rates of the processes responsible for change in concentration of substances, internal and external substance flows in various parts of the investigated ecosystem, and turnover time of all chemical and biological components considered in model (Leonov 2008).

2.4 Hydrodynamic Models of Marine Environment

Time scales of biochemical transformation of oil products in marine environment amount months, years, and in some cases decades. At the same time, having appeared in water, oil spill undergoes the shorter-term transformations (hours, days) caused by synoptic variability of hydrometeorological and hydrodynamic conditions in the basin and over its aquatory.

In the late twentieth century, owing to use of advanced measuring equipment and adequate space–time measuring strategy, the qualitatively new data on structure, synoptic and mesoscale variability of hydrophysical patterns in the World Ocean have been obtained. The real dynamic state of marine aquatories is determined by such processes as synoptic eddies, fronts, meanders of currents, shelf wind currents. Herewith, the progress in weather forecast reached by modern atmospheric models, allows using the modeling parameters of surface layer in dynamic models of the ocean in real time mode (unlike prescription of climatic atmospheric fields practiced in the 1960s–1980s). Thus, now there are prerequisites for creation of joint dynamic models of ocean and atmosphere and their coupling, capable of reproducing the state of marine environment hydrodynamics and, consequently, investigating dynamics of its oil and chemical pollution at synoptic time scales.

Over the last thirty years various aspects of the problem of accidental oil spills in the sea are discussed at annual international conferences “Oil Spill Conference” held in the USA. During the first decade after sensational wreck of tanker *Torrey Canyon* a great attention was given to study of physical and chemical oil transformation. Today it is uncontroversial that, when investigating oil behavior in the sea, first of all it is necessary to consider the following processes:

- surface oil transport under the combined effects of wind, waves and currents;
- surface oil spreading;
- turbulent diffusion of oil at sea surface and in water column;
- oil evaporation under natural conditions;

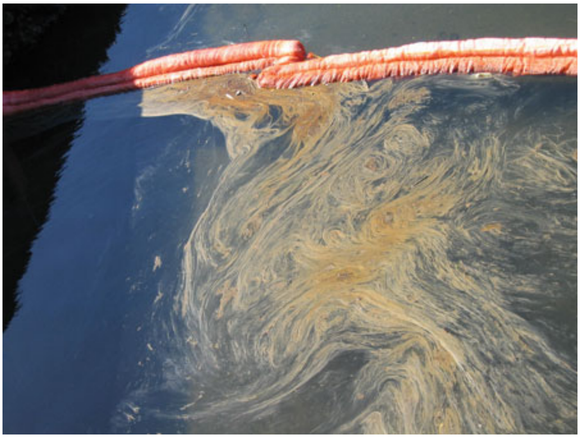

Photo 2.6 Along with processes of transport, spreading, dissolution, and evaporation of oil, hydrodynamic models describe its emulsification—formation of "chocolate mousse" [www.inapcache.boston.com]

- oil penetration in water column from the air-sea interface as droplets;
- formation of water-in-oil emulsion, "chocolate mousse" (Photo 2.6).

Thus, the adequacy of physical and mathematical models of oil spreading after accidental spill depends on the level of our knowledge of hydrophysical, hydrochemical and hydrobiological parameter distribution in specific place and time. At present, degree of exploration of the mentioned processes is different. For some of them the mathematical models corresponding to the present level of physical ideas have been already formulated, for others only empirical parameterizations or qualitative representations exist.

Nevertheless, the Oil Spill Models are created and used for various calculations and forecasts worldwide. Currently the most known models include: American OILMAP-WOSM (Worldwide Oil Spill Model) (Anderson et al. 1995), ADIOS (Automated Data Inquiry for Oil Spills), and GNOME (General NOAA Oil Modelling Environment); American–Norwegian COZOIL (Coastal Zone Oil Spill Model) (Hewlett and Jayko 1998); British OSIS (Oil Spill Information System) (Leech et al. 1993), and Russian SPILLMOD (Oil Spill Modelling) (Ovsienko et al. 2005).

Model OILMAP-WOSM (Worldwide Oil Spill Model) was created by request of American oil companies and today is used by them in those areas, where the companies have business. At calculations in parameterized form the processes of oil spreading, evaporation and dispergation are considered. Model COZOIL has "grown" from the same "incubator" as OILMAP and developed by joint efforts of the American and Norwegian specialists. Today this model is the most complicated by its architecture, as it includes block for calculations of coastal wave dynamics and uses the knowledge of morphological features of coastal zone and offshore strip.

Model OSIS differs principally from the above two models by method of mathematical description of oil spreading because oil spill in this model is represented as an ensemble of oil droplets of different size which in the process of modeling sink into the water column and then rise to the surface under buoyancy force, participating simultaneously in diffusional dispersion and transfer in the upper mixed layer of the sea.

2.4.1 Russian Hydrodynamic Model of Oil Spills "SPILLMOD"

To date the Russian model SPILLMOD has rather wide geography of application both in Russia and international projects. The main model feature is associated with computing technology allowing estimating the change in configuration of oil spill and its properties in the area with arbitrary geometry of contacting boundaries. Unlike other known models, in SPILLMOD the processes of oil spreading and transport are calculated "hydrodynamically" but not "parametrically" that allow reproducing the oil spill dynamics most adequately. The computing algorithms allow to consider almost all known processes of oil spill transformation and to include the operations on mechanical oil recovery (oil skimmers), use of chemical dispersants, localizations of oil with booms, oil combustion in the model. It is notable that since 1998 the model is a basis of computer simulators of Marine Academy of US Coast Guard, developed by British company TRANSAS MARINE.

For the Caspian Sea, for example, the program complex SPILLMOD includes models: circulation dynamics, sea ice dynamics, joint model of circulation and ice dynamics, models of wind wave and dynamics of oil spill with processes of its physical and chemical transformation.

The possible directions of oil spill model application are—forecast of accident occurred previously—retrospective forecast (calculation) for analysis of accident consequences—estimation of hypothetical accidents for assessment of possible consequences—training of specialists with use of computer simulators of accident— development and selection of effective strategies of application of technical means for localization and elimination of oil spill accidents.

2.4.1.1 Accident Simulation

In most cases accidents at sea occur under the severe hydrometeorological conditions, and time for decision making on specific response measures is limited. For this reason the preliminary estimated scenarios of possible accident development can provide actual benefit. Modeling of oil spreading gives a possibility to assess the probable scales of damage for marine environment before accident initiation. By results of computer simulation the experts engaged in development of oil spill response (OSR) plans, can draw conclusion on how resources and facilities for prevention or minimization of resultant emergencies should be organized, and models of spill technology application allow assessing various strategies of oil localization and minimization of accident consequences.

Having used, for example, the data of geographic and ecological model of the Kerch Strait as source information, in 2006 we implemented 16 prognostic numerical calculations (scenarios) of oil spill transformation under the influence of physical and dynamical processes with the SPILLMOD model (Fashchuk et al. 2007) (see Fig. 1.16, Chap. 1). Similar calculations were made for the northeastern Sakhalin shelf (Ovsienko et al. 2005).

Figure 2.1 demonstrates another example of model accident simulation–estimation of oil stain configuration forming under different wind situations in 2 h after the 1500 ton oil spill during transfer operations in the terminal area of port of Tuapse (Black Sea).

2.4.1.2 Identification of Risk Zones and Probability of Object impact by Oil Spill in the Aquatory or in Coastal Zone of the Sea

The risk zone of object impact in the aquatory or in coastal zone over the certain periods of time is an important statistical characteristic of possible oil spreading area. Figure 2.2 shows embedded areas, boundaries of which can be reached by oil spill if the response measures have not been taken.

The technique of risk zone construction consists in the following. The aquatory around a source is divided into subareas or cells of rectangular grid with sides such as all oil slick motion trajectories would enter the selected zone. Then, for each grid element the minimum time, necessary for oil spill to enter the specified cell is estimated. By the obtained grid dataset the contours of areas or risk zones, where oil spill can appear within the chosen timeframes or, in other words, transport of oil spill outside the corresponding zones in specified time is unlikely, are constructed.

The probability of object impact within a certain zone can vary in wide range and depends on time since accidental oil spill, relative positions of accident source and impacted object, linear and area characteristics of protecting object, volume and regime of oil dumping. As a rule, the conditional probability of object impact, i.e. *provided* that spill has occurred, is calculated. The probability of occurrence of oil spill of various volumes is calculated at estimation of industrial risk.

Figure 2.3 shows distribution of impact probability of the 10 km “squares” on the aquatory at volley of oil in the Varandey terminal area of the Pechora Sea and conventional point 8 in the Baltic Sea.

2.4.1.3 Forecast of Development of Accident Situation After Oil Spill

The operational forecast of situation development is an important element of the negative consequence prevention management system of actual (already happened) accidental oil spills in the sea. The *forecast* of oil slick motion trajectory and changes in characteristics of oil or oil products allows setting the

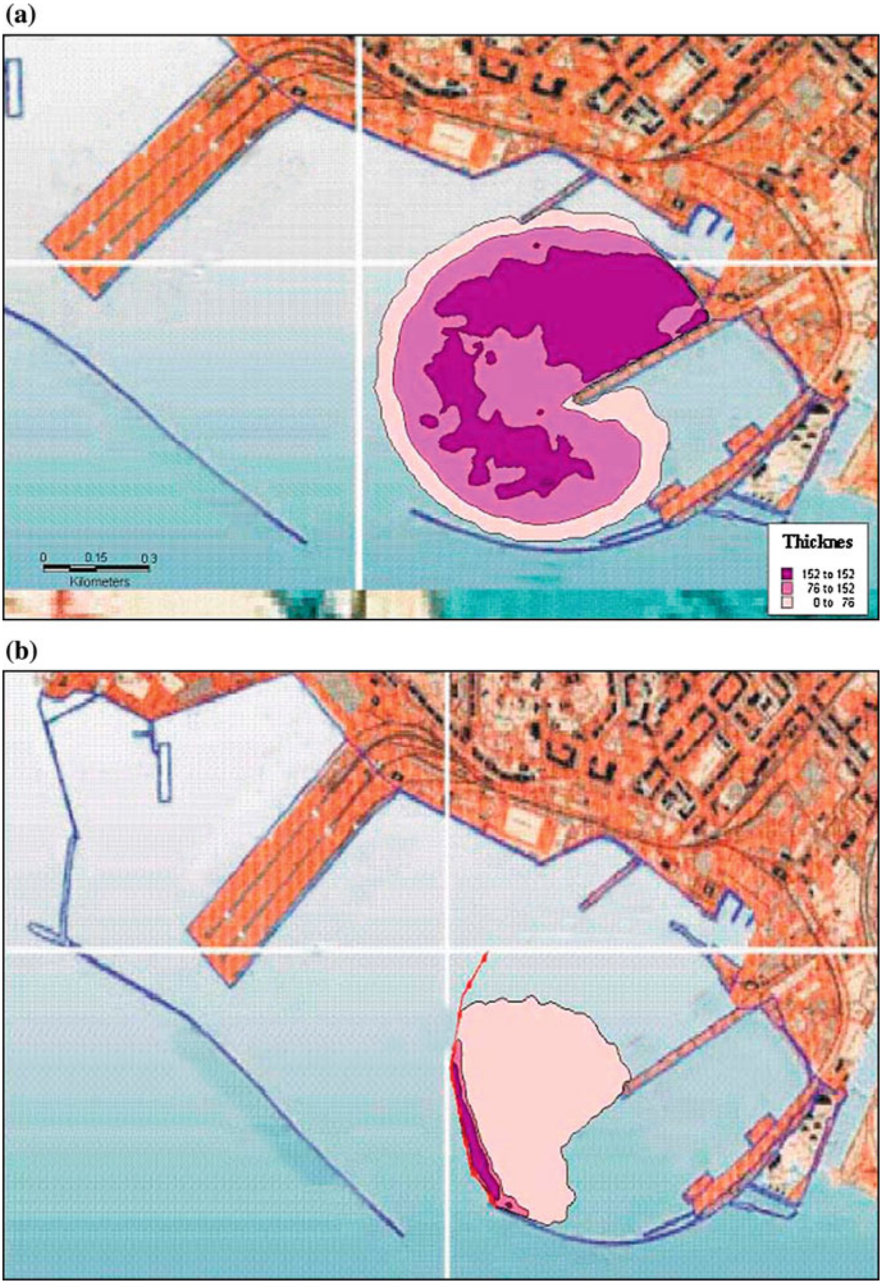

Fig. 2.1 Scenario of oil stain transformation (thicknes of oil film, micron) in 2 h after the 1,500 ton oil spill in port of Tuapse (Ovsienko et al. 2005) (Wind: **a** still; **b** northeast, 6 m/s)

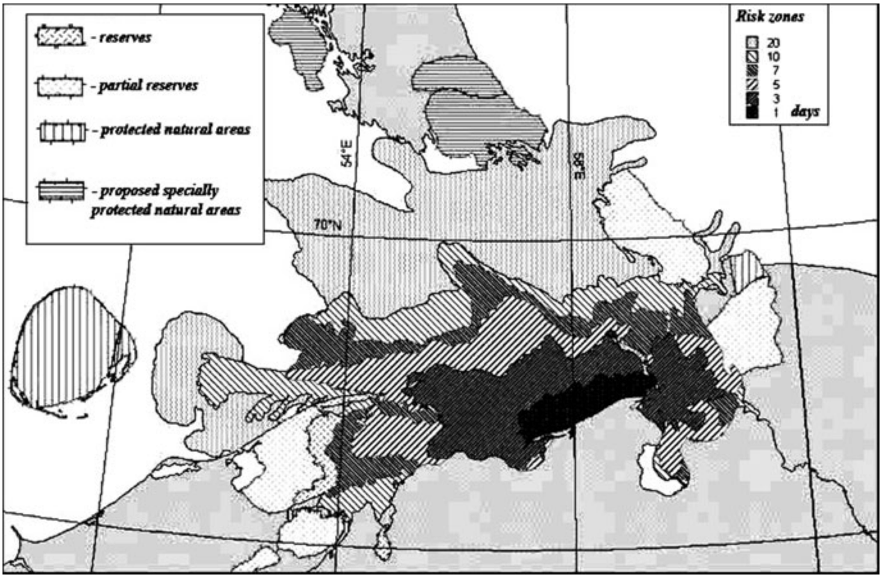

Fig. 2.2 Risk zones of oil spreading at accident in the area of Varandey terminal (Pechora Sea) (Ovsienko et al. 2005)

effective response measures. For these purposes the program complex SPILLMOD, based on the system of mathematical models describing main hydrometeorological processes which determine oil behavior in marine environment, can be used also.

The first version of model SPILLMOD developed in 1990, has been used in real-time regime for the forecast of development of catastrophic crude oil spill in the Persian Gulf during military operations in January–February, 1991 when within four days about 6 million barrels of oil were dumped from several points of the Kuwait coast into the northwestern Persian Gulf. Three months after the estimations their results were compared with satellite observations in the military zone. Despite the limited set of input data, the results of comparison have appeared rather encouraging (Fig. 2.4).

2.5 Conclusions

Using the methods of mathematical modeling, based on the system interrelated description of chemical, biological and physical processes (geographic and ecological information models), the problems of the long-term chemical composition of natural waters and its long-term changes in space and in time are studied. Moreover, on the basis of current information, numerical methods and computing

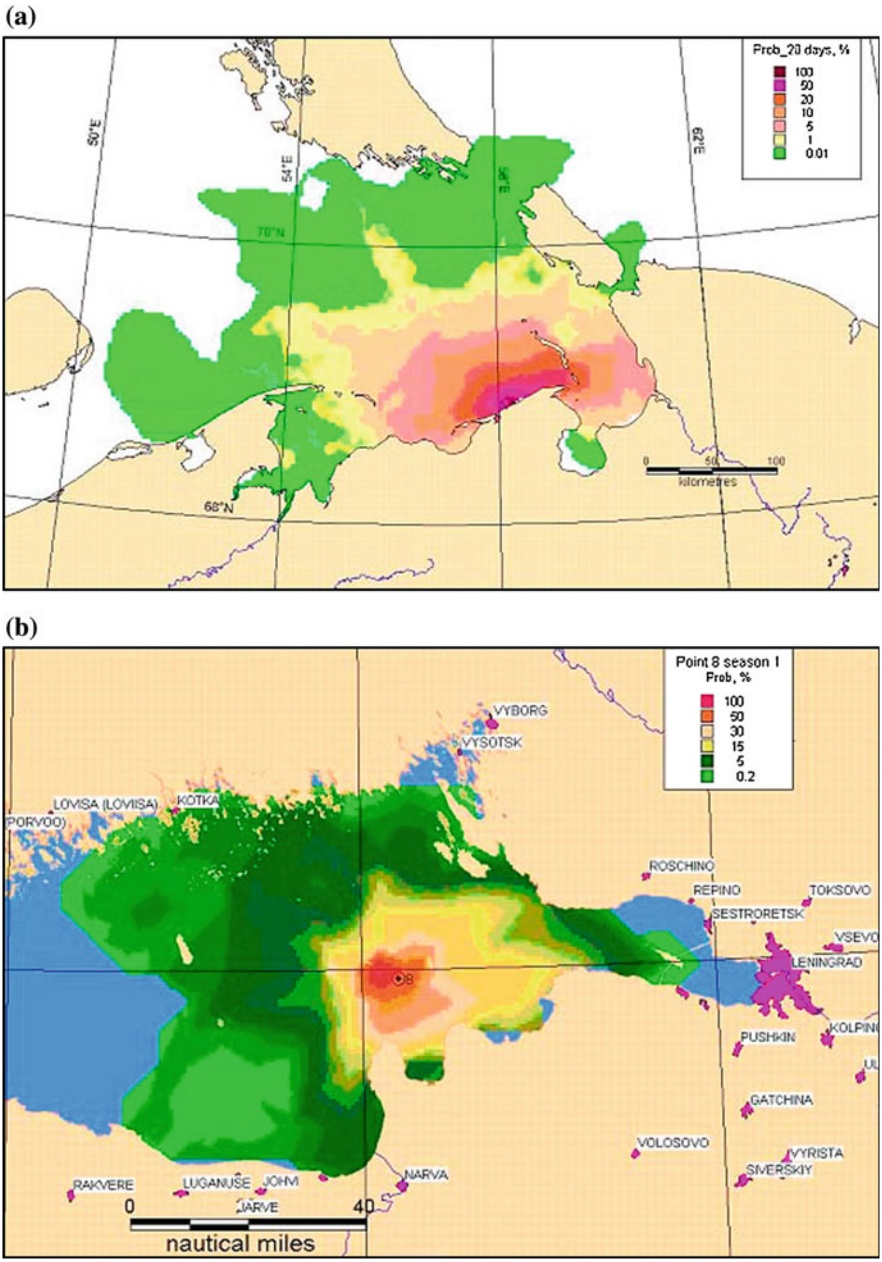

Fig. 2.3 Probability of marine aquatory impact as a result of oil volley in the Varandey terminal area of the Pechora Sea (**a**) and in the zone of hypothetical oil spreading in the Baltic Sea (**b**) (Ovsienko et al. 2005)

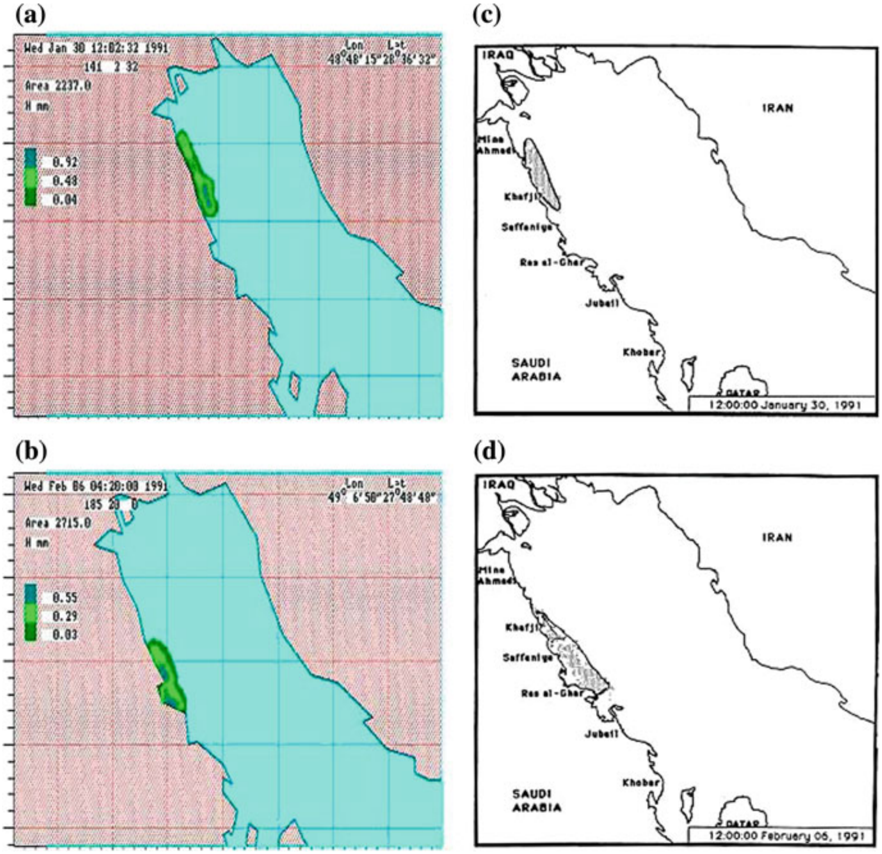

Fig. 2.4 Model calculations of oil spill dynamics in the Persian Gulf (**a**, **c**) and its actual position by satellite observations (**b**, **d**) (Ovsienko et al. 2005)

facilities, the mathematical models, capable of describing the main dynamic processes in the ocean at synoptic spatiotemporal scale are created.

In prospect, this apparatus can be applied to control of the water body state, tracing of anthropogenic factor role in formation of water resource quality, properties of natural waters in specific water bodies and streams, and also in different basins and aquatories of marine ecosystems. In particular, the investigations seem rather actual at solving of the environmental problems, planning of nature protection actions, rationalization of use of biological and mineral resources of the Caspian, Barents, Black, White, Okhotsk, and other Russian seas with account of the forthcoming development of their shelf oil and gas fields, building of terminals and ports for treatment and transportation of oil hydrocarbons.

Today, for the known economic reasons the complex observations on the state of ecosystems of these basins practically are not conducted or have episodic character. In these circumstances, the methods of mathematical modeling get a special applicability. On the basis of available scarce and irregular information, they allow:

- assessing the volumes of nutrients entering into the water basin with river discharge, atmospheric precipitation, and as a result of interchange at the water-bottom interface;
- assessing the ecosystem response on variations in intensity of these sources by change in nutrient flows due to development of biotransformation processes (nutrient uptake, elimination of metabolic products, die-away of hydrobionts, intensity of trophodynamic interactions) and under the transfer of water mass components across the boundaries of adjacent aquatories;
- assessing the eutrophication effects by increase in hydrobiont biomass, intensity and duration of phytoplankton blooming, changes in conditions of nutrient limitation of bioproduction processes (P or N);
- assessing the intensity of vertical transfer and nutrient and organic matter exchange between the upper and deeper sea layers, conditions of oxygen deficit formation in the near-bottom water;
- identifying and assessing quantitatively the role of main biological components participating in production cycle and favoring the redistribution of nutrient forms in water column by their intraaanual supply and subsequent biotransformation in marine ecosystem;
- defining the priority processes determining the production capacity of marine basins and, on this basis, providing recommendations on their rational natural resource use and environment protection;
- studying the dynamics of oil spills under the influence of hydrometeorological factors;
- making the model reconstructions of hypothetical oil spill dynamics under the different scenarios of synoptic situations, ice conditions, real coastal orography and seafloor topography.

Mathematical modeling of marine ecosystems on the basis of adequate data of geographic and ecological information models—"portraits" is one of the prospective lines of marine ecological geography.

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Chapter 3
Hydrogen Sulphide Zone in the Open Black Sea: Mechanisms of Formation, Evolution, Dynamics and Present State

According to present ideas about the history of our planet, 400 million years ago the fourth in succession of Monogaea (2.6 billion years ago), Megagaea (1.8 billion years ago.) and Mesogaea–Rodinia (1 billion л.н.) supercontinent Pangaea (from the Greek meaning "all land"), or Wegener's Land, has split into two near the equator. As a result, two continents were formed: Gondwana included Africa, Hindustan, Antarctica, Australia and the South America, in the south, and the Northern continent which initially represented the underwater margin (shelf) of Pangaea. About 280 million year ago, having risen above the sea surface, it formed Laurasia separated from Gondwana by the ancient Tethys Ocean (Sorokhtin and Ushakov 2002).

At final stages of its development in the beginning of Cenozoic Era, 45–35 million years ago (Late Eocene), the southern margin of Lavrasia in the area of present basins of the Mediterranean, Black and Caspian Seas represented a series of marginal water reservoirs separated from the ocean by islands and island arcs (Fig. 3.1a) (Nevesskaya et al. 1984). This system was named Peritethys—periphery of Tethys.

In the Early Oligocene (35–30 million years ago) under the influence of tectonic movements of the Alpine belt (Alpine orogenesis) caused by convergence of continental plateaus of Africa, Arabia and Hindustan with Eurasia, the northern Tethys margin was isolated from the main ocean, having formed a huge inland reservoir of Paratethys, parallel to Tethys (Fig. 3.1b). In latitudinal direction it stretched between 40° and 50° N, from the northern piedmonts of the Alps in the west to foothills of the Tien Shan (Fergana valley) in the east. By its extent the Paratethys exceeded the present Mediterranean Sea by a factor of 1.5 (6,000 km), and by the area—not less than in 2 times (3.4 million km^2).

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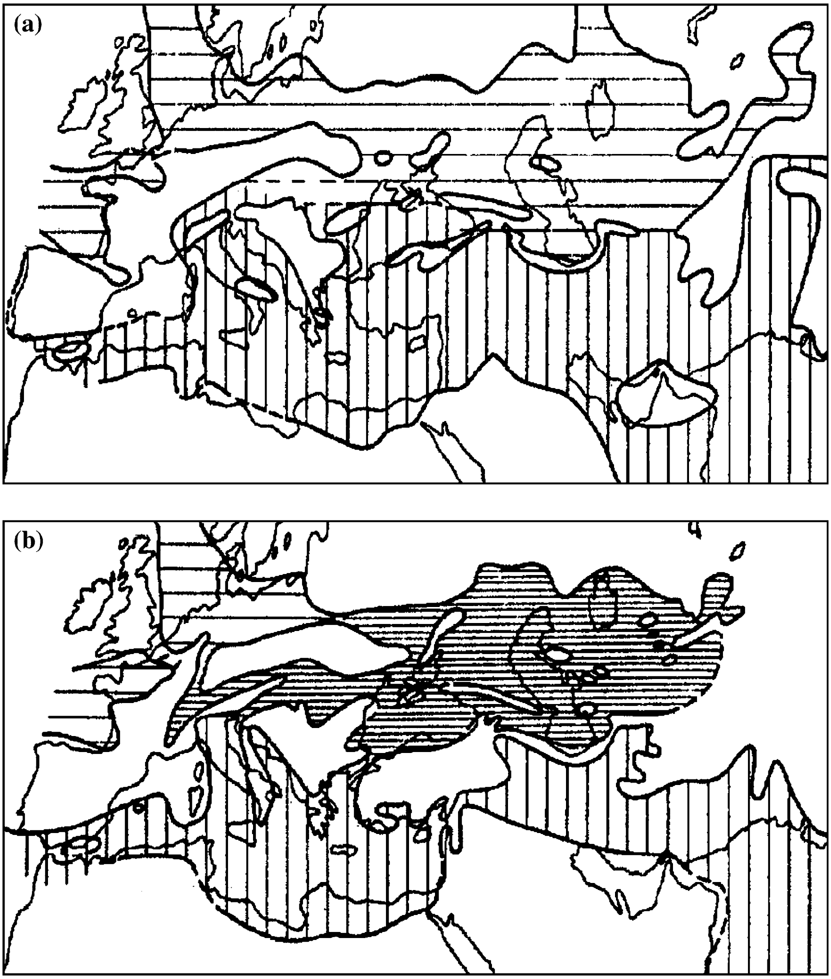


Fig. 3.1 Paleoreconstructions of acient basins of the Caspian, Black and Mediterranean Seas 45–35 (**a**) and 35–30 (**b**) million years ago (Nevesskaya et al. 1984) (Hatching: vertical—Tethys Ocean; light horizontal—Peritethys; dense horizontal—Paratethys)

3.1 Paleoreconstructions of Ancient Basins of the Black Sea

During the following more than 30 million years (Oligocene, Neogene) the Paratethys experienced at least seven cycles of development when its connection with the World ocean interrupted or revived, and, consequently, salinity and species composition of organisms varied (Fig. 3.2a–f).

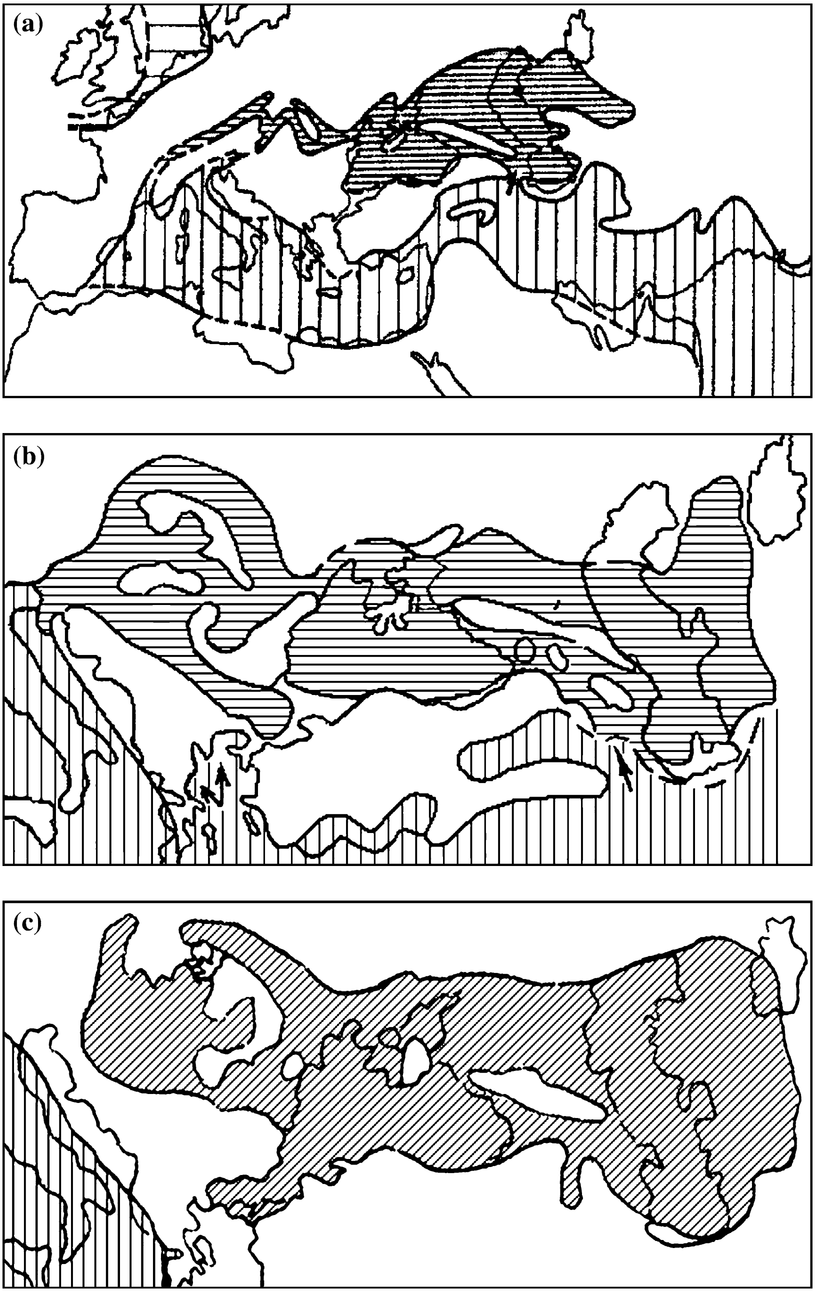


Fig. 3.2 Paleoreconstructions of evolution of the Paratethys basin (Nevesskaya et al. 1984); **a**, **b**, **c**, **d**, **e**, **f**—20–16; 16–12; 12–8; 7; 6–5; 3.5–1.8 million years ago, respectively (Descriptions as in Fig. 3.1; *Crosshatching*—semi-marine; *dots*—brackish-water; *arrows*—possible connection to open ocean)

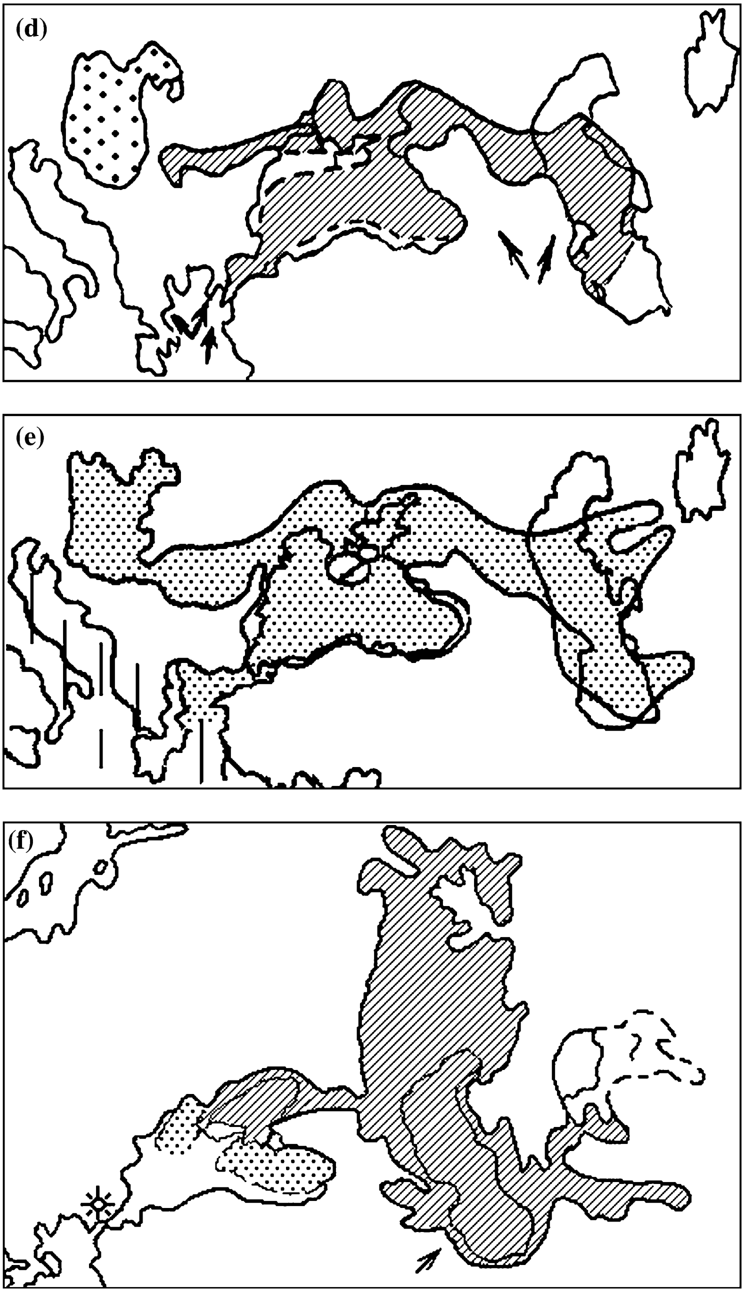


Fig. 3.2 (continued)

3.1.1 Evolution of the Paratethys Basins

3.1.1.1 Cycle I

In the beginning of its history, 35–30 million years ago, the Paratethys was connected with the Atlantic Ocean through the strait stretched from the Baltic Sea across the territory of Ukraine (Fig. 3.1b). Its salinity was high that resulted in progressive development of the near-bottom hydrosulfuric zones. Scientists believe that presence of the strait between boreal reservoirs (ancient Atlantic) and the Paratethys explains the nature and composition similarity of Cenozoic amber deposits in the Baltics and East Europe. Amber was carried across the sea—strait from the northwestern basin to the east (territory of Ukraine) by monsoon “amber winds”.

3.1.1.2 Cycle II

At the end of the Early Miocene (20–16 million years ago) the Paratethys started to split into the West (Pannonian) and East (Euxine–Caspian) basins, the latter exceeding the counterpart more than twice by its size (Fig. 3.2a). During this stage the connection of the Paratethys to the World Ocean (Atlantic) continued, its salinity was close to oceanic, and development of hydrogen sulfide zones reached its maximum that was reflected in basin fauna—for the period of 25–20 million years ago it remains unknown. At the end of the cycle the basin was isolated from the ocean and freshened.

3.1.1.3 Cycle III

In the beginning of the Middle Miocene (16–15 million years ago) the Paratethys was split distinctly into the East and West basins. Therewith, the first basin continued to isolate from Tethys waters, while the West basin kept the connection to it both in the southwest (with Mediterranean) and in the southeast (with Indo-Pacific) via the East Mediterranean (the Trans-Caspian, East Georgia) (Fig. 3.2b). The third development cycle for the East Paratethys was ended in the late Middle Miocene (13–12 million years ago) with formation of the *Karaganian* basin, completely isolated from the ocean, with salinity lower than in the sea. 12–11 million years ago the East Paratethys was connected to the ocean (via East Turkey or Iran) for short period again. In this *Konka* period its salinity rose up to oceanic values, and the basin was inhabited by euryhaline species. The coastal configuration was changing, and new endemic and unique species developed actively (Photo 3.1a–e).

3.1.1.4 Cycle IV

Then 11–10 million years ago the connection of the West Paratethys to the ocean discontinued, and it was transformed to a series of fresh-water and brackish-water

Photo 3.1 Relicts of preglacial epochs: terebinth (*Pistacia mutica*)—(**a**), Grecian strawberry tree (*Arbutus andrachne*)—(**b**), Greek juniper (*Juniperus excelsa*)—(**c**), and Stankewicz pine (*Pinus stankewiczii*)—(**d**, **e**), remain a visiting card of the modern South Coast of Crimea (Photo: www.tour/crimia.com)

basins. The vast (from the Carpathians to Turkmenistan) semi-closed *Sarmatian* basin remained in place of the East Paratethys, connected periodically to the Mediterranean (Fig. 3.2c). Throughout the whole period its salinity decreased (down to 3–4‰) that eventually (9–8 million years ago) led to extinction of marine organisms.

3.1.1.5 Cycle V

In the middle of late Miocene (7 million years ago) the *Meotic* stage of the Paratethys development associated with new marine transgression, began. During this period the basin area reduced. The basin is believed to contact with the Mediterranean at that time via the Euphrates Strait named so by A.L. Chepalyga, who was the first scientist to find its fossil evidence in the territory of modern East Turkey. The alternative communication between the East Paratethys and might be realized via the areas of Macedonia, Thrace, and European Turkey (Fig. 3.2d). By the end of the Miocene period (6 million years ago) salinity of the Euxine-Caspian basin started to decrease because of its growing isolation.

3.1.1.6 Cycle VI

In the end of the late Miocene—beginning of early Pliocene (6–5 million years ago) after the next transgression, the Paratethys changed into the brackish-water Early Pontian basin consisted of a number of isolated water bodies: the Pannon, Dacia, Euxine, Caspian, and Aegean basins (Fig. 3.2e). The reason of transgression could consist in the strengthening of communication between the basin and Mediterranean Sea because of tectonic faulting and growth of river discharge as a result of climate change.

In the beginning of late Pliocene (3.5 million years ago) the Euxine basin, having passed several stages, became a source of the present Black Sea. In the eastern Paratethys the sea retracted in the limits of the present Middle and South Caspian, lost its connection with the Euxine basin and formed the basin of the future Caspian Sea.

At the first stage of the *Caspian* basin development pool it represented only a southern depression, with the Volga, Samura, Kura, Uzboy Rivers running into it. Naturally, the water body was almost fresh with a massive layer of deltaic deposits of “productive stratum” which for millions of years have buried immense oil reserves in their layers. It is curious that the nature of these resources (deposits of deltaic vegetation) differs from the nature of the North Caucasian oil fields. The latter appeared much earlier in deeps of the ancient H_2S-containing Meotic basin.

3.1.1.7 Cycle VII

In upper Pliocene (~3.5–1.8 million years ago) the Caspian area descended, and waters of the young Caspian basin spread mainly northward, having formed the *Akchagylian* basin characterized by rather high salinity of oceanic type as a result, as the authors believe, its communication with the Mediterranean via the already mentioned Euphrates Strait (Fig. 3.2f).

3.1.2 Quaternary Basins of the Black Sea

In the Quaternary period (last 1.8 million years) the transformation of basins of the southern seas started 35–30 million years ago, continued (Chepalyga 2002). Herewith, in the Black Sea temperature, salinity and species composition of inhabitants varied the utmost, while the level changed slightly. In the Caspian Sea the salinity jumps were smaller, and the level changes—more noticeable. Under the influence of tectonic processes and periodic climate shifts, the communication between basins and with the Mediterranean via the Bosporus and Manych was often broken, and at coast of the southern seas and in the basins themselves the unique environmental conditions were formed. The results of their paleoreconstructions obtained by different authors generally coincide but there are also some contradictions indicating the broadest field of work in this domain for the future researchers.

The beginning of the newest, Quaternary, history of the Black Sea basin is associated with the longest, so-called Chaudinian transgression began about 1 million years ago and lasted more than 500,000 years. During this period the Black Sea was connected for the first time with the Caspian Sea, and the one-way water flow of the latter into the Sea of Azov which at that time represented a shallow liman of the Pontus, began. Thus, the Black Sea from the almost isolated Gurian pool formed by that time as a result of the Paratethys evolutions, transformed into a large brackish-water reservoir (10–15‰).

After the next regression the level of the new, *Chaudian* basin lowered by 70–80 m compared with the present, and its salinity started to increase as a result of penetration of more saline Mediterranean waters into the Black Sea plain via the Bosporus, having reached the current values of 19–20‰ by the end of early Pleistocene (500–350 thousand years ago).

In the beginning of the XX century (1903) one of the paleoecology founders academician Nikolay Ivanovich Andrusov (1861–1924) discovered Chaudin brackish-water mollusks on the Dardanelles coast. They were found also in deltaic sediments of the Danube and Dnieper where at that time under the influence of deep penetration of sea waters into river valleys the extensive saline (10–15‰) lagoons exceeded the present ones in 1.5–2 times by their area, were formed. Therewith, the coastal line was located by 10–15 m above the present level, and the climate was warm and wet, close to subtropical. The basin coast was represented by forest-steppe landscapes with broad-leaved forest vegetation –oak, hornbeam, linden, ash tree, hazelnut (Svitoch et al. 2000).

The next stage of the Black Sea history began in the early Middle Pleistocene (350–300 thousand years ago) when after the Ancient Euxine transgression the reservoir became a brackish-water marine basin connected with the early Khazar Caspian Sea through the Manych trough. From the Chaudin transgression it was separated by the period of sea level lowering (by about 60 m) and freshening to 10‰. Nevertheless, by the end of the *Ancient Euxinian* period salinity of the Black Sea increased again, up to 17‰.

The further basin development continued during the periods of the *Uzunlarian* (~300–200 thousand years), *Karangatian* (130–80 thousand years), and *Tarkhankutian* (40–14 thousand years) transgressions, when the Panticapean basin of Mediterranean type has existed in its place. In the *Uzunlarian time* the regional climate was cooler, compared with the Ancient Euxine epoch, but lukewarm, with the tendency toward aridity strengthening. Salinity of the sea rose up to 19‰, its level was by 4–5 m higher than at present, connection with the Caspian Sea was episodic but that with the Mediterranean Sea strengthened. The basin size did not exceed the present.

In the *Karangatian period* lasted 50 thousand years (130–80 thousand years ago) the Black Sea area reached 4,500 km^2, salinity in its open part—30‰, and the sea level exceeded the present value by 6–8 m. Through the deeply eroded (to –100 m of datum) Bosporus huge volumes of warm, saline Mediterranean water entered the basin (Fig. 3.3; Photo 3.2). As a result, sea waters spread up the river valleys by tens of kilometers. The Manych trough became a broad, long (~200 km) estuary turned periodically into the strait between the Black and Caspian Seas. Therewith, the climate continued to be warm and temperate arid. Further, during more than 60 thousand years, the reservoir level lowered gradually. As a result, its communication with the Caspian and Mediterranean Seas weakened (35–25 thousand years ago), and salinity decreased to 8‰.

At the end of late Pleistocene (18 thousand years ago) the sea was completely isolated from other inner basins. The next, *New Euxine* stage of its development caused by the Wurm—Valdai glaciation and, correspondingly, deep regression (fall of level mark to—90–110 m of datum) has come. The ancient coastal lines (18–17 thousand years) off the South Crimean Coast are found at depths of 80–100 m.

At the end of last glaciation (17–15 thousand years ago) in the period of warming maximum the huge volume of water from melting glaciers of Scandinavia and permafrost occupying the whole Russian Plain up to the southern seas at that time, filled the Aral and Caspian basins during hundreds of years. Then, through the Manych trough and Kerch Strait the Khvalyn (Caspian) Sea rushed in the Black Sea, then through the Bosporus—in the Sea of Marmara, and via the Dardanelles—in the Mediterranean Sea. Such paleoreconstruction suggested by A.L. Chepalyga is confirmed by discovery of ancient (15–16 thousand years) submerged delta from the southern side of the Bosporus (Sea of Marmara), deposits of which contain Caspian mollusks of the same age (Fig. 3.4).

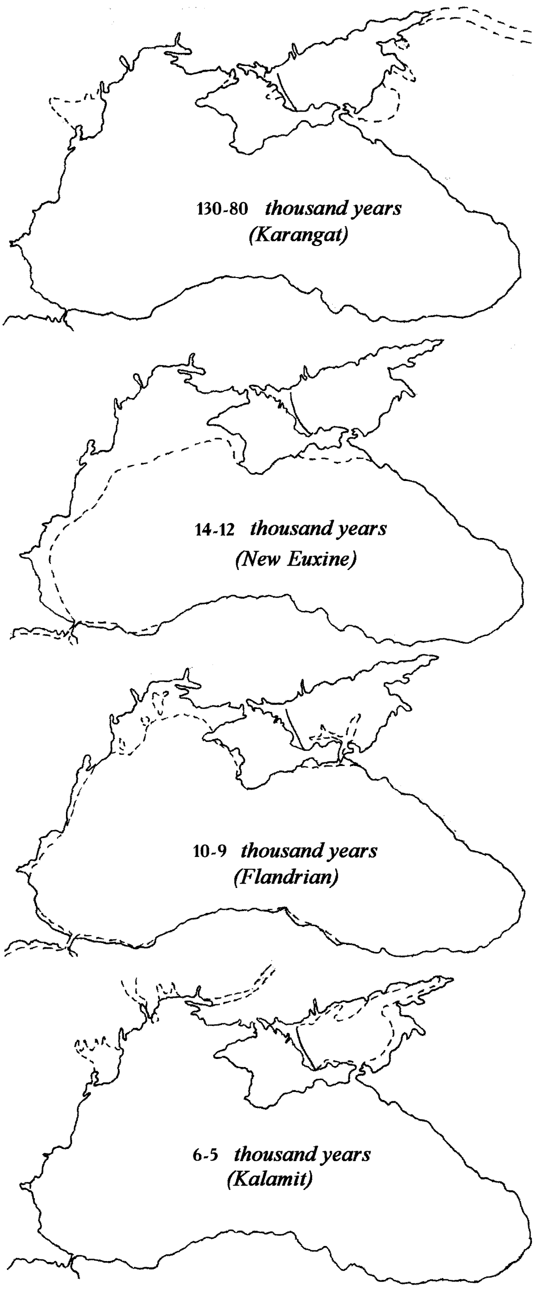


Fig. 3.3 Ancient Quaternary basins of the Black Sea (by Chepalyga 2002). *Continuous line* present contours of the Black and Azov Seas; *dashed line* paleoboundaries of ancient basins

Two thousand years on the period of the next sea level fall began (14–12 thousand years ago) during which the Sea of Azov shrank (Fig. 3.3). Its bottom represented a low coastal plain crossed by the Don valley. The river delta was

Photo 3.2 Ancient coastline of Karangat basin of the Black Sea (130–80 thousand years ago) at outcrop of the Taman Coast of the Kerch Strait (light horizon in the middle part of scarp—at the *top*) and fossil seashells from this horizon (*bottom*) used for paleoreconstructions (photo by A. Chepalyga)

located 50 km south of the Kerch Strait. Mouths of the Dnieper, Dniester and Danube merged, forming one delta—the vast canyon at distance of 200 km from their present position. Thus, the Kerch Strait and Bosporus did not exist during that period. The valleys located in their place served for drainage of the ancient Don and New Euxinian basin fresh waters.

The final *Flandrian* stage of the Black Sea evolution was associated with the next Holocene transgression caused by "rush" of Mediterranean waters through the Bosporus (Fig. 3.3). According to some data, it occurred 8–7, according to other—15–12 thousand years ago. After that the basin level started to rise and 9–8 thousand years ago in the formed *Bugaz–Vitiazian* (10–9 thousand years ago) sea it reached the present isobaths of 30–35 m. Further, in the process of filling with saline water, the New Euxinian sea-lake turned into a semimarine two-layer H_2S—containing *Kalamitian* reservoir (6–5 thousand years ago) with salinity of 19‰ in the open aquatory, 7–12‰ in the near-mouth areas and lagoons, and up to 20–22‰ in the near-bottom layer of deepwater basin (Fig. 3.3). In the late Holocene (4–3 thousand years ago) level of the new

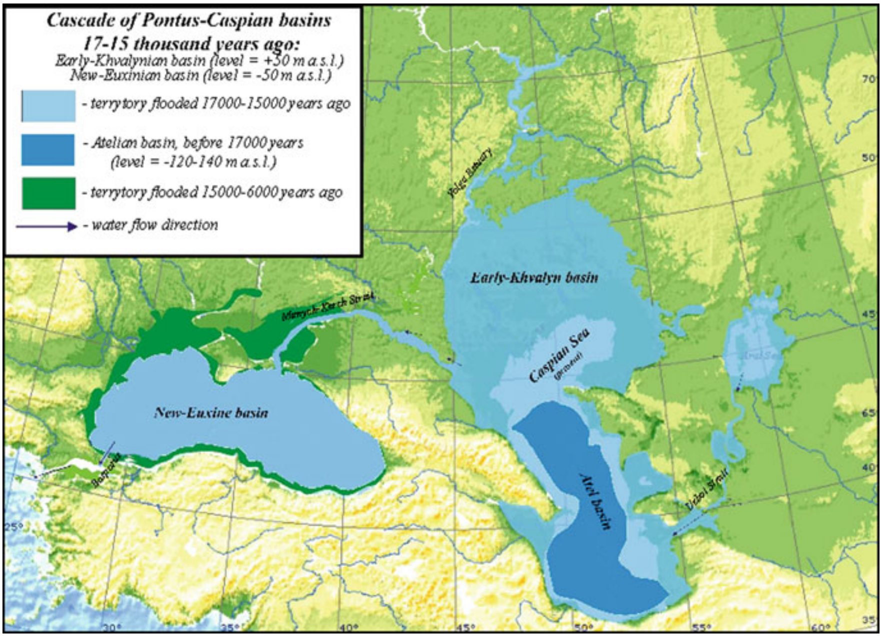
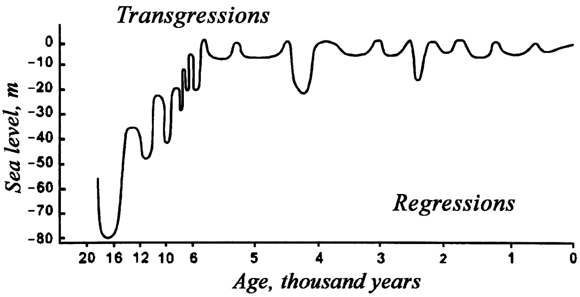


Fig. 3.4 Paleoreconstruction of connection of the Pontic—Caspian basins in the Late Glacial Period and Holocene (Chepalyga 2005)

Fig. 3.5 The Black Sea level changes in the Late Glacial Period and Holocene (Chepalyga 2002)



Jemetin Sea reached +1 to +2 m of datum, and ecological conditions in the *New Black Sea* basin became close to present.

It should be noticed that the Quaternary history of the Black Sea formation was not so rhythmical and "regular" as it may seem from the suggested scheme. Apart from the described long-term stages of its existence, there is an evidence of at least five shorter transgression–regression periods in the basin, alternated over the past 10,000 years because of climate and tectonic activity changes (Fig. 3.5).

During these periods the average volume (545–547 thousand km^3) and area (400–421 thousand km^2) of the Black Sea changed inappreciably. Nevertheless, by some estimates over the last 7 thousand years during the *Holocene* transgression the basin could renew its waters about 10 times. And the volume of the Sea of Azov under such level fluctuations increased to 340–428 thousand km^3 in the transgression periods and decreased to 40–252 thousand km^3 at retreat of the sea.

3.2 Mathematical Modeling of Evolution of Hydrological and Hydrochemical Structure of the Black Sea Waters

The above—presented results of paleogeographic reconstruction of ancient Black Sea basins, coupled with similar datings of their age and quantitative characteristics of marine environment conditions obtained by authors of other interdisciplinary studies (Arkhangelsky and Strakhov 1938; Vinogradov et al. 1962; Deuser 1974; Shimkus et al. 1973; Fedorov 1980; Shcherbakov 1982; Sorokin et al. 1984; Yeremeev et al. 1994; Yeremeev and Sovga 1999; Nikolaev 1995; Neretin et al. 2001; Svitoch 2003, etc.), have formed quite certain ideas about the history of the Black Sea evolution, mechanisms of generation and development of anaerobic conditions in it.

The primary cause of anaerobic condition formation in the deep-water part of the world's largest H_2S-containing reservoir ($\sim$467 thousand km^3—90% of the sea volume) consists in peculiarity of its hydrological structure and salinity regime forming under water exchange with the Sea of Marmara via the Bosporus and climatic factors (river runoff, precipitation).

Inflow of saline (34–36‰) Marmara Sea water into the Black Sea along the Bosporus bottom (Lower Bosporus Current), started 13.5–7 thousand years ago (Nikolaev 1995) and continuing today (Table 3.1), has led over time to formation of vertical salinity (density) gradient between surface water freshened by river runoff and precipitation and deep, more saline water at intermediate depths. This density stratification—"hydrological cover", became a barrier to inter-layer mixing and oxygen penetration into the basin deeps (Boguslavsky et al. 1980).

After formation of the described hydrological structure of the Black Sea water the oxygen consumption for oxidation of organic matter under its weakened penetration into the deep layers due to mixing and absence of photosynthesis there resulted in development of hypoxia, up to a complete disappearance of dissolved oxygen in basin deeps. Under these conditions the aerobic—anaerobic interface ("redox-cline") located in the upper sediment layer at presence of oxygen in

Table 3.1 Some components of the Black Sea water balance (km^3/year) (Project "Seas … 1991a, b)

Component	Statistical characteristic			Fluctuations range of mean values
	Min	Mean	Max	
River runoff	246	338	492	328–348
Inflow via the Bosporusp	96	176	274	171–178
Outflow via the Bosporus	250	371	540	362–380

water, shifts into the water column. The sulfate reduction process, i.e. anaerobic oxidation of organic matter by sulfate–reducing bacteria consuming sulfate oxygen in the process of their activity, thus disoxidating sulfur compounds and producing hydrogen sulfide, begins there (Skopintsev et al. 1961). The studies of sulfur isotope composition (^{32}S and ^{34}S) in deepwater sediments of the Black Sea allowed to suggest that sulfate reduction has started after the beginning of the New Euxine basin transformation (salinity rise) (Vinogradov et al. 1962; Volkov 1991).

Existence and dynamics of the upper anaerobic zone boundary were determined in the following by intensity of hydrogen sulfide oxidation with oxygen in the layer of their coexistence (C-layer)—a contact zone of aerobic and anaerobic waters. The intensity of this chemical process, in turn, depends on volume of oxygen and hydrogen sulfide fluxes (mass transfer) into the C-layer, concentration of reagents, and presence of catalysts in water. The activity of hydrogen sulfide oxidation is affected also by ions of metals with variable valency (*Ni*, *Co*, *Mn*, *Cu*, *Fe*), phosphates, organics, and pH of the environment.

The estimations of generation time, chronology of hydrological structure formation and evolution of the Black Sea anaerobic zone made without considering their genetic linkage and features of hydrogen sulfide production and oxidation differs essentially (Deuser 1974; Skopintsev 1975; Hay 1988; Yeremeev et al. 1994). Moreover, the analysis of results of investigations on formation conditions of salinity regime in the Black Sea by methods of mathematical modeling (Aizatulin et al. 2003), carried out by many authors (Boguslavsky and Kotovshchikov 1984; Yeremeev et al. 1996; Boudreau and Leblond 1989; Mamaev 1994) without considering the results of paleogeographic reconstructions (choice of initial and boundary conditions), showed that such simulations produced a picture inadequate to the ancient basin nature established with the use of paleogeographic data.

3.2.1 Formation of Vertical Salinity Profile

In the early XXI century a team of authors from Institute of Oceanology and Institute of Geography of the Russian Academy of Sciences under the direction of T.A. Aizatulin, after the analysis of results of paleogeographic reconstructions of the Quaternary basins of the Black Sea, real sizes and values of its water balance components, ran model calculations of evolution of salinity and vertical turbulent oxygen exchange conditions in the Black Sea, having used the methodology and mathematical apparatus of the predecessors (Boguslavsky and Kotovshchikov 1984; Yeremeev et al. 1996; Mamaev 1994). Herewith, the initial and boundary conditions for calculations included the initial value (10.5‰) and vertical distribution of salinity and salinity of the Lower Bosporus Current water (35‰) in the New Euxine period, water volumes in separate layers of the Black Sea, components of water balance (river runoff, volumes of the Lower and Upper Bosporus Currents) have been defined not abstractedly as earlier but using the real data taken from the composed geographic and ecological information model (Aizatulin et al. 2003).

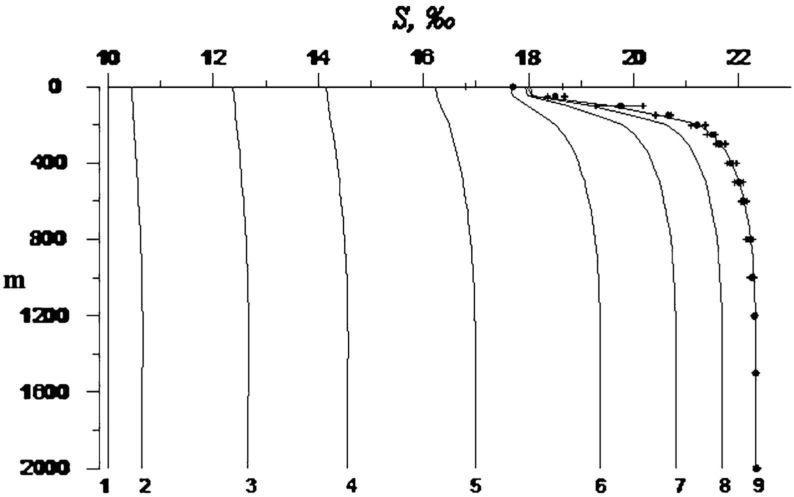


Fig. 3.6 Calculated profiles of vertical salinity distribution in the Black Sea at different stages of salinity structure evolution (Aizatulin et al. 2003) (*1* initial salinity distribution; *2–9* the same but 100, 500, 1000, 2000, 4000, 6000, 7500, and 8600 years after the beginning of water exchange via the Bosporus. Dots on profile 9—present averaged salinity values in the Black Sea from (Project "Seas… 1991a, b))

As a result of the calculations, the evolution of salinity profiles in the Black Sea was reproduced at initial salinity of the Lower Bosporus Current of 35‰ and volumes of river runoff, inflow and outflow via the Bosporus close to the present values (Fig. 3.6).

The model reproduced the present salinity profile (curve 9) *8600 years* after the beginning of the Lower Bosporus Current. In the 0–100 m layer the calculated salinity values fell in the observed fluctuations range but at the surface they were by 0.3‰ above the long-term mean. At depths from >100 m to the bottom the calculated salinity profile reproduced completely the present mean long-term vertical distribution of this characteristic in the basin (Project "Seas… 1991a, b).

By results of model calculations of evolution of the Black Sea salinity profiles during the past 8600 years the dynamics of intensity of its waters mixing for this period was investigated—values of the coefficient of vertical turbulent exchange (K_z), inversely proportional to vertical salinity (density) gradient, were calculated. It emerged that even at small vertical salinity differences a layer of low K_z values—a zone of difficult vertical transfer, "blocking layer" (curve 1, Fig. 3.7), was formed at shallow depths of the Black Sea as early as the first hundred years after the Bosporus "outbreak".

At the later stages of basin evolution, with strengthening of salinity stratification in the sea, the K_z value in the "blocking" layer has started to decrease, reaching its minimum at present time (curve 6, Fig. 3.7). Herewith, it occupies depths between 100 and 200 m, i.e. those where the upper boundary of the Black Sea anaerobic zone is registered today.

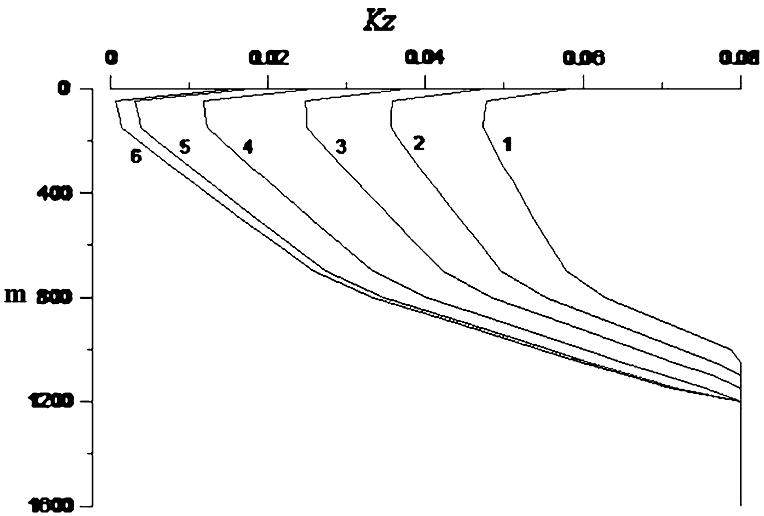


Fig. 3.7 Calculated profiles of the coefficient of vertical exchange K_z (cm^2/s) (Aizatulin et al. 2003) (*1–6* profiles 100, 500, 1000, 2000, 4000, and 8600 years, respectively, after the beginning of water exchange via the Bosporus)

Thus, mathematical modeling of vertical salinity distribution in the Black Sea, based on the data of geographic and ecological information model, allowed to prove that evolution of the basin salinity structure (for the past 8600 years) was accompanied by formation of characteristic profiles of the coefficient of vertical turbulent exchange in it, with a minimum in the 100–200 m layer, "blocking" oxygen penetration into the deep sea.

3.2.2 Generation and Development of Anaerobic Conditions

The quantitative estimations of variability of vertical transfer intensity in the Black Sea and ideas about the basic physical—dynamical and biochemical mechanisms determining formation of its oxygen regime presented in Sect. 3.2.1, allowed developing the mathematical model of anaerobic zone evolution—a dynamics of oxygen and hydrogen sulfide concentrations, position of its upper boundary at different stages of the basin geological history (Aizatulin and Leonov 1990).

In the suggested one-dimensional model the development of anaerobic zone is associated with:

- processes of salinity structure formation in the basin, depending on variability of water balance components;
- processes of vertical water exchange and diffusive transfer determining transport of oxygen and hydrogen sulfide into the water column;
- redox processes of the oxygen–hydrogen sulfide interaction in the layer of their coexistence on the upper boundary of anaerobic zone.

The diffusive oxygen flux from the atmosphere, its inflow with river discharge and outflow with waters of the Upper Bosporus Current were defined as surface boundary conditions. The absence of oxygen sources and prescribed hydrogen sulfide flux from the bottom (sulfate reduction rate in the near-bottom layer) were set as bottom boundary conditions. Moreover, the rate of hydrogen sulfide oxidation in the coexistence layer (C-layer) on the upper boundary of anaerobic zone was specified as proportional to reagent concentrations. The oxygen reserve in the surface layer is replenished not only through exchange with the atmosphere and inflowing river waters but also due to Marmora Sea water of the Lower Bosporus Current at intermediate depths of 200–1500 m. Oxygen is consumed in the process of dissolved organic matter oxidation. The model was run until the complete reproduction of present hydrogen sulfide profile corresponding to mean conditions of salinity stratification formation over 8600 years after the beginning of salinization of the sea.

According to results of model calculations (Aizatulin et al. 2003), the total depletion of O_2 in the 1900–2000 m layer has occurred for ~3.455 thousand years after the beginning of salinization of the sea (continuous curve with the date of 3.455 in Fig. 3.8). By this moment a rather thick layer of "salinity jump" (see curve 6 in Fig. 3.6) has been already formed in the surface horizons, where the vertical turbulent exchange (see curves 4, 5 in Fig. 3.7) slowed down insomuch that oxygen penetration into the deep layers was practically terminated.

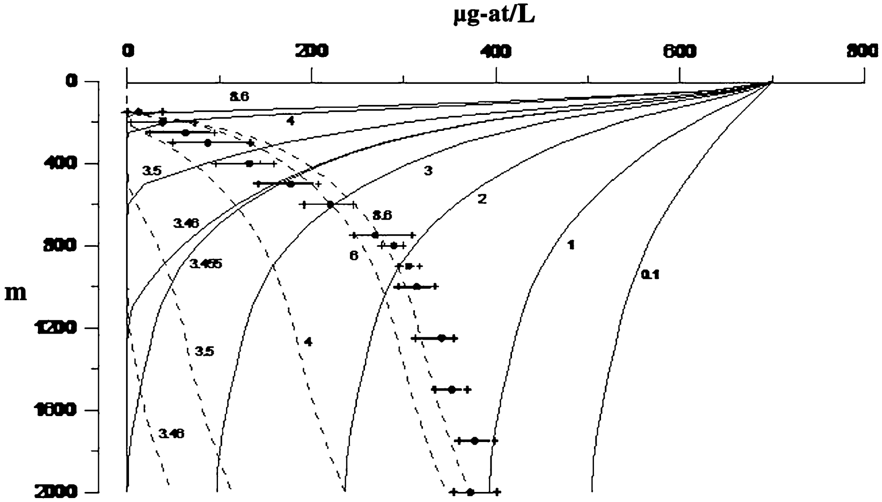


Fig. 3.8 Calculated profiles of oxygen (*continuous curves*) and hydrogen sulfide (*dashed line*) concentrations in the Black Sea at different stages of its anaerobic zone formation (Aizatulin et al. 2003) (Figures at curves—time (thousands of years) after the beginning of water exchange via the Bosporus. Black circles—present mean long-term concentrations of hydrogen sulfide and their fluctuations range at different depths, from (Project "Seas… 1991a, b))

The disappearance of oxygen in the 100-m near-bottom layer resulted in rapid development of sulfate reduction, production of hydrogen sulfide, there. As late as 5 years the anaerobic zone was generated at depths from 1000 m to the bottom (dashed curve with the date of 3.46 in Fig. 3.8). After 45 years the upper boundary of hydrogen sulfide has rose up to 500 m, and after 500 years (4000 years after the Bosporus outbreak) it has reached a depth of 200 m.

At the initial stage of hydrogen sulfide generation in the Black Sea (3.455–3.46 thousand years) its oxidation developed in the 900–2000-m layer. In the subsequent period (3.46–4 thousand years) the upper boundary of the layer of their coexistence (interaction) rose up to 160 m, and its lower one—up to 1100 m. Hereafter (4–8.6 thousand years), the layer of oxygen–hydrogen sulfide interaction occupied boundaries of 140–700 m. Thus, at early stages of the Black Sea salinity structure formation, until the coefficient of vertical exchange has reached the certain critical value, the oxygen–hydrogen sulfide interaction occurred in thick water column (1100–940 m). With that, the upper boundary of hydrogen sulfide rose rapidly because of the prevalence of its diffusive upward flow over oxygen downward flow. 4 thousand years after, when salinity stratification in the Black Sea was completely set, the zone of oxygen–hydrogen sulfide interaction was shrunk and limited to depth range of 150–300 m (period of 4–6 thousand years), and then—to a layer of 150–200 m (period of 6–8.6 thousand years). With that, a rise of its upper boundary was slowed down because by that time the diffusive oxygen flows into the C-layer, according to model calculations, began to exceed the hydrogen sulfide transport there by factor of 1.8–30.4.

According to the model calculations made on the basis of geographic and ecological information model, the present anaerobic zone of the Black Sea was generated for 5.145 years, in the period from 3455 to 8600 years after outbreak of the Bosporus. In the last 3600 years the diffusive oxygen flow (downwards) in the Black Sea was balanced by hydrogen sulfide flow (upwards) and development of oxidizing processes in the layer of their coexistence (130–170 m). As a result, the equilibrium of reagent flows into the C-layer, determined the stabilization of position of the Black Sea anaerobic zone upper boundary, was established.

3.3 Hydrogen Sulfide Zone of the Black Sea

The centuries-old history of the Black Sea existence contains many examples of disasters and transformations connected with tectonic movements, climate and ocean level changes. Their consequences were manifested in periodic transformations of the reservoir from freshwater, completely aerobic basin into the saline, H_2S—containing basin, and vice versa. During the last 3 thousand years the nature in this region was relatively stable, and at present, under the influence of historically developed physico-geographical features, the Black Sea is the second-largest H_2S—containing sea basin of the World Ocean after the Cariako Trench.

From the first determination of hydrogen sulfide concentration in Black Sea water in 1891 till 1960 observations on this characteristic have been carried out in several stages and had irregular character both in time and space episodic expeditions of the Imperial Russian Geographical Society, conducted in 1890–1900 under the guidance of N.I. Andrusov, sea field investigations of the Azov-Black Sea Fisheries Research Expedition, Main Hydrophysical Department and Sevastopol Biological Station of Academy of Sciences of the USSR during 1923–1935 under the direction of N.M. Knipovich and Yu.M. Shokalsky, results of works of Azov-Black Sea Research Institute of Fisheries and Oceanography conducted in 1938–1949 under the direction of Ya.K. Gololobov, observational data obtained in 1951–1960 by B.A. Skopintsev and Yu.I. Sorokin from Institute of Oceanology of Academy of Sciences of the USSR, and many other known investigators of the sea allowed to get a certain idea about the nature of hydrogen sulfide zone of the Black Sea, regularities of its dynamics.

Since 1960 divisions of Main Department of Hydrometeorological Services of the USSR have organized regular observations on hydrogen sulfide distribution in the Black Sea on standard horizons of 75, 100, 150, 200, 300, 400, 500, 600, 800, 1000, 1200, 1500, and 2000 m under the scheme of stations included 4 secular cross-sections. Samples from the 100 m depth have started to be taken from 1963, and those from the 75 m horizon—since 1969 (Ryabinin and Kravets 1989). In 1974–1978 and 1979–80 the scheme of stations has been changed for various reasons, and only since 1981 the sampling locations have become stationary. By the end of the XX century the bank of data on hydrogen sulfide content in the Black Sea have included more than 16,000 measurements obtained at 2300 stations in 96 expeditions from 1960 to 1986.

The above-noted vertical discreteness of observations does not allow defining the exact position of hydrogen sulfide upper boundary, which is most often located between standard horizons. Thus, despite the availability of hydrogen sulfide data bank, there is no long-term time series of observations on position of its upper boundary in the Black Sea now. The special investigations with sampling every 5–10 m, necessary for this, were carried out incidentally in 1938–1949 and 1950–1960, had local character. Thus, they cannot be used for statistical estimations. Results of the listed works made over more than centennial period, are contained in numerous articles and monographs. By the end of the XX century the collected data led many researchers to believe that the Black sea was one of the most studied basins of the World Ocean. Nevertheless, incidents of the last decades of the XX century show that it is far from true.

3.3.1 Nature and Spatiotemporal Distribution of Hydrogen Sulfide

The first organoleptic (by means of nose) hydrogen sulfide determinations in the Black Sea were made by boatswain of Russian Navy gunboat *Chernomorets* during expedition of Russian Geographical Society, organized by N.I. Andrusov, I.B. Shpindler, and F.F. Vrangel, in summer, 1890. Having smelt ground and water samples taken from the bottom, the brave sailor has reported enthusiastically to its head N.I. Andrusov: "Stinks, your Nobleness!". N.I. Andrusov published information about this fact in Proceedings of Russian Geographical Society (Andrusov 1890). Hereafter, the disputes on, where hydrogen sulfide in the Black Sea deeps comes from and what prevents its penetration into the upper layer of the basin, have started, resembling a detective story.

In 1893, investigating the Black Sea hydrogen sulfide origination during the next expedition, organic chemist N.D. Zelinsky established that its source in the sea was associated with microbiological sulfate reduction in the presence of organic matter. He investigated sulfate-reducing bacteria *Bacterium hydrosulfureum Ponticum* and studied "release of H_2S by our microbe" (Zelinsky 1893).

In 1895, explaining the reasons preventing the hydrogen sulfide penetration into the upper layers of the Black Sea, M.A. Egunov, on the basis of laboratory trials with silts and mud from the Odessa limans (estuaries), Lake Nero near Rostov Yaroslavsky, Siberian and Crimean salty lakes, stated a hypothesis: "*at depth of about* 200 m *the whole Black Sea is crossed by a zone filled with sulfur bacteria…, assimilating hydrogen sulfide to such an extent that there is no any trace of this gas in the surface layer*" (Egunov 1900). According to the author's suggestion, the area of "bacterial slice" can reach 330 thousand km^2. Search for the film of microorganisms assimilating hydrogen sulfide in the Black Sea have been conducted without result for more than 50 years.

N.M. Knipovich, agreeing with a certain contribution of bacteria to hydrogen sulfide oxidation, assumed that "*boundaries of hydrogen sulfide area are determined by oxygen content*" (Knipovich 1930). This point of view was shared by known microbiologist B.L. Isachenko (Isachenko and Egorova 1939). After unsuccessful search for "film" he suggested that "*It is a vertical circulation that prevents hydrogen sulfide penetration into the upper layers… owing to this process… an oxidation of hydrogen sulfide by dissolved oxygen can occur*", i.e. by chemical means. In the following, it was proved by hydrochemists (Skopintsev 1953; Skopintsev et al. 1961; Bruevich 1953).

It is fair to say that unsuccessful search for the "Egunov's film" have been far from so useless. In these expeditions microbiologist A.E. Kriss found the huge number of thionic bacteria oxidizing hydrogen sulfide and other sulfur compounds in the upper ground layer at depths of more than 2000 m. At the upper boundary of hydrogen sulfide zone they concentrated only as individual cells (Kriss and Rukina 1949).

In the 1960s–1970s, after application of a new technique, Yu.I. Sorokin established that thionic bacteria constituted a basic mass of microorganisms in the water layer between aerobic and anaerobic zones of the sea (Sorokin 1962).

The first quantitative determinations of hydrogen sulfide in the Black Sea were made by analyst of Novorossisk University A.A. Lebedintsev on the expedition under the guidance of I.B. Shpindler, organized by Main Hydrographic

Department of the Russia on board R/V *Donets* and *Zaporozhets* in 1891. They allowed to conclude that the upper boundary of anaerobic zone was located at depth of 100 fathoms, or 183 meters. This idea persisted for more than 30 years (Lebedintsev 1892).

Only in the late 1920s the investigations conducted under the direction of N.M. Knipovich and Yu.M. Shokalsky showed that position of the upper boundary of hydrogen sulfide in the Black Sea was not stable. Chemists of the mentioned expeditions P.T. Danilchenko and N.I. Chigirin stated (Danilchenko and Chigirin 1926) that "*it varies substantially in relation to the sea area, possibly due to currents, and season, depending on vertical circulation*".

While accumulating the experimental data on hydrogen sulfide nature, its concentrations and character of spatial distribution in the Black Sea, by the end of the XX century the majority of investigators of this problem have developed the following ideas:

- the basic part (99,5%) of Black Sea hydrogen sulfide is formed as a result of sulfate reduction by (sulfate-reducing) bacteria utilizing sulfate oxygen under decomposition of organic matter in anaerobic conditions below pycnocline, while only 0,5% of H_2S are formed due to putrefactive disintegration of sulfur-containing organic compounds;
- content of sulfate-reducing bacteria in water column is small, and maxima of their assemblies (intensity of H_2S production) are located in the upper part of the H_2S-containing water layer (down to 300 m) and in the near-bottom layer;
- despite the fact that intensity of sulfate reduction in sediments is 10–100 times higher than in water, the total production of hydrogen sulfide in water column due to this process is 5–20 times large (because thickness of deep water layer exceeds that of sedimentary layer by factor of 100–1000);
- to date, despite the intensive expedition research, a strong evidence of endogenic (abiogenic) origin of hydrogen sulfide in the Black Sea (from the Earth's interior with juvenile water or at submarine discharge of hydro-therms) has not been obtained;
- mean concentration of hydrogen sulfide increases steadily with depth and reaches maximal values in the near-bottom layer (2000 m), which in the long-term context (1960–1985) are equal to: 7.9 mL/L in winter, 8.7 mL/L in spring, 9.75 mL/L in summer, and 8.30 mL/L in autumn (Ryabinin and Kravets 1989);
- in all seasons the coefficient of variation of hydrogen sulfide concentrations is maximal at depth of 150 m (110–130%) and decreases down to the bottom (2000 m) to 10–14% (Table 3.2);
- mean long-term distribution of hydrogen sulfide at depths from 150 to 2000 m (Fig. 3.9) is in agreement with the generalized scheme of water circulation in the Black Sea (see Fig. 1.12);
- despite the consensus regarding the H_2S genesis, until now the estimates of total annual production of hydrogen sulfide in water column, obtained by various authors from direct measurements, *differ by an order—from* 3.6 *to* 85 million t (Bezborodov and Yeremeyev 1993).

Table 3.2 Seasonal concentrations of hydrogen sulfide (mL/L) at different depths of the Black Sea for the 1960–1985 period (Ryabinin and Kravets 1989)

Season	Depth	Mean	Min	Max	σ	C_v (%)
Winter	150	0.10	0.00	0.52	0.13	130
	200	0.40	0.00	1.10	0.32	80
	250	0.85	0.00	2.00	0.41	55
	300	1.30	0.00	2.89	0.52	40
	400	1.88	0.58	3.10	0.50	27
	500	2.72	1.38	3.68	0.60	22
	800	4.52	1.97	6.23	0.72	16
	1,000	5.10	2.72	6.98	0.68	13
	1,500	6.00	4.25	7.70	0.60	10
	2,000	6.44	4.56	7.90	0.70	11
Spring	150	0.13	0.00	0.80	0.15	115
	200	0.49	0.00	1.42	0.32	64
	250	0.90	0.00	2.25	0.42	50
	300	1.37	0.02	3.10	0.47	34
	400	1.96	0.48	3.67	0.48	27
	500	2.90	0.81	4.56	0.60	21
	800	4.63	1.50	6.14	0.79	17
	1,000	5.33	2.00	6.51	0.72	13
	1,500	6.00	2.94	7.23	0.66	11
	2,000	6.60	4.40	8.70	0.80	14
Summer	150	0.20	0.00	1.50	0.18	130
	200	0.55	0.00	2.56	0.27	66
	250	0.92	0.00	2.00	0.35	53
	300	1.38	0.29	3.83	0.36	26
	400	2.04	0.38	3.92	0.45	22
	500	2.94	0.44	5.77	0.52	18
	800	4.88	0.85	6.27	0.76	16
	1,000	5.54	1.60	7.29	0.75	14
	1,500	6.44	2.50	8.50	0.80	12
	2,000	7.10	3.80	9.75	1.10	16
Autumn	150	0.16	0.00	0.83	0.18	110
	200	0.53	0.00	1.65	0.33	62
	250	0.95	0.00	2.00	0.40	49
	300	1.39	0.20	2.30	0.43	28
	400	1.98	0.36	2.98	0.50	24
	500	2.90	0.70	3.92	0.58	20
	800	4.72	2.08	5.90	0.79	17
	1,000	5.35	2.27	7.11	0.79	14
	1,500	6.30	3.48	7.48	0.80	13
	2,000	6.68	3.73	8.30	0.95	14

3.3.2 Topography of the Upper Hydrogen Sulfide Boundary and its Determining Factors

As a result of numerous field investigations, it is established that the boundary of the Black Sea anaerobic zone coincides with the upper boundary of water layer, in

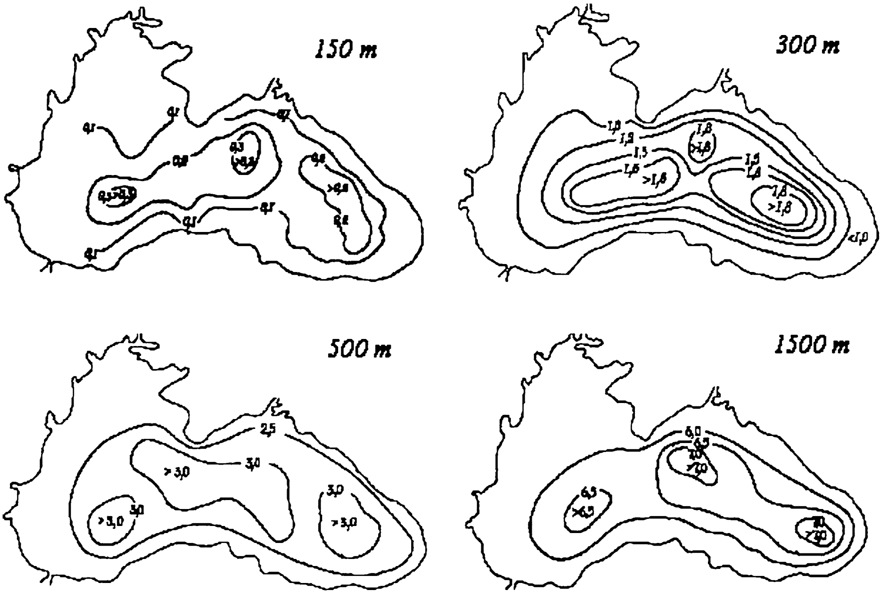


Fig. 3.9 Mean long-term (1973–1985) fields of hydrogen sulfide concentrations (mL/L) in the Black Sea at different depths (Ryabinin and Kravets 1989)

which oxygen and hydrogen sulfide are present simultaneously in very low concentration—a layer of their coexistence (C-layer).

In terms of ecology the C-layer is a main zone, in which the balance of hydrogen sulfide is realized, i.e. the zone where its chemical and bacterial oxidation preventing the penetration of H_2S-containing water into the upper layers of the basin, occurs. Hydrogen sulfide oxidation in the C-layer is realized in two stages: at first it is oxidized chemically to thiosulfate and sulfate in the ratio of 1:1, and then generated thiosulfate is finally oxidized by thionic bacteria to sulfate. The rate of oxidation is proportional to concentrations of reacting components (Sorokin 1982). Moreover, the C-layer is the main boundary for penetration of life of higher (compared with bacterial) trophic levels into the deep layers of the sea.

Despite the arisen disagreements (after application of new methods of sampling and hydrogen sulfide and oxygen determination in the zone of their coexistence) concerning the vertical size of the C-layer (up to denial of fact of its presence) and, consequently, the integral rate of H_2S oxidation in it (Bezborodov and Yeremeyev 1993), most authors recognize the existence of this surface in the Black Sea.

By discrete data obtained in the 1920s–1930s by N.I. Danilchenko, N.I. Chigirin, N.M. Knipovich, the hydrogen sulfide boundary in the Black Sea was located at depths of 100–125 m (Danilchenko and Chigirin 1926; Knipovich 1932). B.A. Skopintsev and his colleagues found it at the same depth in the early 1950s (Skopintsev and Gubin 1955). In summer, 1961 at single stations hydrogen sulfide was registered at depth of 85–90 m (Vinogradov 1962), in spring, 1969—at

75 m (Timoshchuk and Risik 1980), and at the same depth—in December, 1977 and in August, 1978 (Ryabinin and Kravets 1980).

As a result of the mentioned observations, it was concluded: *position of the hydrogen sulfide zone boundary in the Black Sea is not stable, it varies considerably, depending on the sea area and season. The form of its relief—dome-like with convexity in the centre of the sea and deepening on periphery, is determined by the general character of circulation (cyclonic) ensuring downwelling on the basin periphery and upwelling in its central areas.*

According to data obtained by Ya.K. Gololobov in the 1940s, the thickness of the C-layer varies from 8 to 35 m, and the sea-averaged depth of its upper boundary, depending on season, is 146, 154, 126 and 169 m for spring, summer, autumn and winter, respectively (Gololobov 1953). With that, the form of its relief (dome-like with convexity in the centre of the sea and deepening on its periphery) remains unchanged throughout the year.

3.3.2.1 Intraannual Dynamics of the Hydrogen Sulfide Upper Boundary

In 1982 the Laboratory of the Black Sea Oceanography of Azov-Black Sea Research Institute of Fisheries and Oceanography (today—YuNIRO, Kerch) (Photo 3.3), at the initiative of the author (at that time its employee), started the regular seasonal investigations of the C-layer in the Black Sea at the section from Yalta to Batumi (9 stations every 30 miles)—across the eastern basin, at the latitudinal section from Sochi to Varna (18 stations every 30 miles), and on ecological test sites in the western and eastern parts of the sea. During 1982–1983 in all seasons 128 and 121 stations were made with determination of the depth of C-layer upper boundary (Hs) position (with vertical discreteness of 5–10 m) at the cross-sections (Yalta-Batumi, Sochi-Varna) and on test sites. The total quantity of the O_2 and H_2S measurements in the C-layer was about 1,000 (Fashchuk and Aizatulin 1986).

In July, 1983 on the site in the western sea at 72 stations made every 0.5° of latitude and longitude at standard depths down to 1000 m, we investigated the spatial variability of topography and characteristics of the C-layer (37 stations every 1° by latitude and longitude) and their relation to water circulation structure. The similar dependence was investigated in August of the same year on the site in the eastern sea off Batumi.

Moreover, by data of investigations conducted on the site in the western sea in April, 1979 and 1981 (72 stations every 0.5° by latitude and longitude at standard depths down to 200 m) we estimated the influence of water circulation on dissolved oxygen regime at depth of 50 m.

In 1984–1985 (summer-autumn) these investigations were extended in cooperation with Marine Hydrophysical Institute of the Academy of Sciences of Ukraine—surveys of the H_s topography started to be carried out on the whole aquatory of the sea (40 stations spaced 0.5° of latitude and longitude apart) (Fashchuk et al. 1987).

Photo 3.3 Laboratory of the Black Sea Fisheries Oceanography of AzCherNIRO, Kerch, 1985—(*Lower row*, from *left* to *right*: V.A. Bryantsev (Head of Laboratory), A.Kochergin, T. Tsaturyan, L. Sebakh, T. Petrenko. *Upper row*, from *left* to *right*: D. Fashchuk, L. Voronenko, N. Tovstonos, S. Klimenko, N. Cherkashchenko, N. Kirilova, L. Kovalenko, A. Klyausov, I. Tribrat, T. Pankratova

Surveys on the sites were carried out in 10–12 days, samples for hydrochemical determinations in the C-layer were taken with the Niskin 2-litre vinyl plastic bottles. The hydrogen sulfide concentrations were determined by iodometric method, oxygen in its presence—by the modified Winkler methodology with use of mercury bichloride.

In August, 1982 we registered hydrogen sulfide in the eastern part of the sea at depth of 50 m. Herewith, the profile of the upper boundary of anaerobic zone gave the impression that in the deep of the sea there was a volcanic eruption lifted gigantic cloud of H_2S-containing water into the photic layer (Fig. 3.10,I). The height of hydrogen sulfide dome increased by 70 m for 40 km, its diameter was 120 km, and thickness of the C-layer in the centre reached 150 m. The oxygen concentration in the C-layer ranged from 0 to 1.00 mL/L, that of hydrogen sulfide—from 0 to 0.95 mL/L. In November at the site of “eruption” the upper boundary of the C-layer represented almost flat level surface located at depths of 120–160 m, and its thickness did not exceed 50–60 m (Fig. 3.10,II). At such shallow depth hydrogen sulfide in the Black Sea was never fixed for the whole period of investigations (Fashchuk and Aizatulin 1986).

The shallowest (75 m) position of hydrogen sulfide in the Black Sea was fixed for the first time by specialists of a division of State Committee for

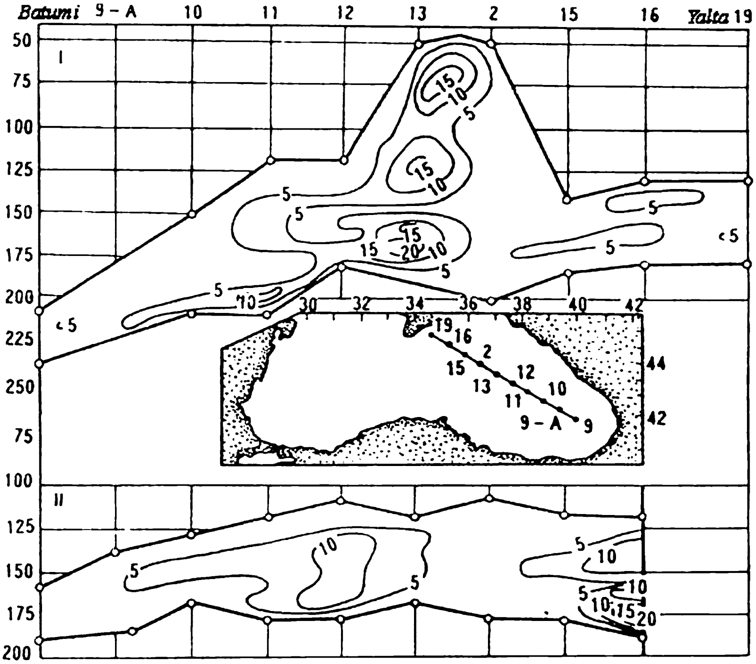


Fig. 3.10 Topography of the upper and lower boundaries of the C-layer and rate of hydrogen sulfide oxidation in it (g m^3/day) at cross-section from Yalta to Batumi in summer (I) and autumn (II), 1982 (Fashchuk and Aizatulin 1986)

Hydrometeorology of the USSR (L.M. Alekseeva) at two stations off Sevastopol in 1964. Its concentration was 0.09 mL/L at the dissolved oxygen content of 6.18 and 6.92 mL/L. In February and May, 1969 at four stations in the eastern and western parts of the sea hydrogen sulfide was registered in concentrations of 0.02–0.24 mL/L also at high (6.05 mL/L) oxygen concentration. This placed in doubt a correctness of analyses, as in such situations the results for hydrogen sulfide may be overestimated because of “oxidation of iodides in acid medium by air oxygen” (Ryabinin and Kravets 1989).

Nevertheless, in the same 1969 and the next years (1977–1979; 1981–1985) hydrogen sulphide at depth of 75 m was repeatedly fixed in concentrations of 0.05–0.79 mL/L in different areas of the Black Sea during different seasons at low oxygen concentrations also. In 1971–1976 hydrogen sulfide at this depth was never registered, but in 1977 it was fixed there at 28 from 105 stations made on the whole aquatory of the sea. Herewith, the hydrogen sulfide concentrations in the Crimean area (16 stations) were 0.05–0.70, in the eastern sea (7 stations)—0.05–0.10, and in the western sea (2 stations)—0.03–0.05 mL/L. The maximal concentration (0.80 mL/L) at 75 m was noted in 1979 (Ryabinin and Kravets 1989).

Our further studies of topography of the upper boundary of anaerobic zone conducted in 1982–1986 on the sites in the open Black Sea showed that hydrogen sulfide “domes” may appear in any area of the sea, and penetration of hydrogen sulfide up to depths of 75–100 m became a usual event for the basin (Fashchuk and Aizatulin 1986). In distinction from the former ideas, the present boundary of the Black Sea anaerobic zone turned out to be a complicated wave-like surface, which relief is determined by a character of water circulation—development of eddy formations in the sea, their displacements and transformation (Fig. 3.11).

In the Black Sea they penetrate down to depth of 150–200 m, and the lateral size ranges from 60 to 150 km. Thus, against the background of the main current representing two large-scale cyclonic circulations named “Knipovich’s glasses” in honor of the scientist described them first, many mesoscale eddies of different sign are generated and dissipated constantly in the Black Sea (Titov 2002).

In the zones of cyclonic vorticity of circulation where waters move counterclockwise, the boundary of hydrogen sulfide zone can rise up to 60–80 m, while in the downwelling areas (periphery of the sea and the centers of anticyclonic circulations) it deepens down to 190–240 m. So, the average depth of upper boundary of the C-layer in the western Black Sea in July, 1983 was 131 m, varying from 80 m in the zones of upwelling in the centers of cyclonic circulations to 190 m on the periphery of cyclonic formations and on the sites with the cyclonic character of water circulation. The average depth of the C-layer lower boundary at that time was 203 m, ranging from 170 to 245 m. Herewith, the C-layer thickness varied from 45 to 120 m and averaged 72 m, increasing sharply in the zones of cyclonic circulations (see Fig. 3.11).

We fixed also the similar relationship between topography of the upper boundary of the C-layer and water circulation in summer, 1983 on the site in the eastern sea (Fig. 3.12). In the center of cyclonic eddy the anaerobic zone was located 40 m deeper than on its periphery.

By results of investigations conducted by Marine Hydrophysical Institute (Sevastopol, Ukraine) in 1984–1985, the maps of seasonal topography of the anaerobic zone boundary for the whole Black Sea aquatory were composed (Boguslavsky et al. 1985; 1986; 1988). They confirms completely our conclusions about fluctuations range of its position and relationship with water circulation (Fig. 3.13).

3.3.2.2 Assessment of Correctness of Methodology of the Hydrogen Sulfide Upper Boundary Determination

The iodometric method traditionally used for hydrogen sulfide determination in seawater gives the information on the sum of reduced sulfur compounds (hydrogen sulfide, polysulfides, sulfites, thiosulfates), expressed in hydrogen sulfide equivalent. As a result, the position of its upper boundary, even at the more frequent determinations with this method by vertical, proves to be overestimated. During the 44th cruise of R/V *Mikhail Lomonosov* (June-July, 1985) together with specialists from MGI of Academy of Sciences of Ukraine, we made about 100

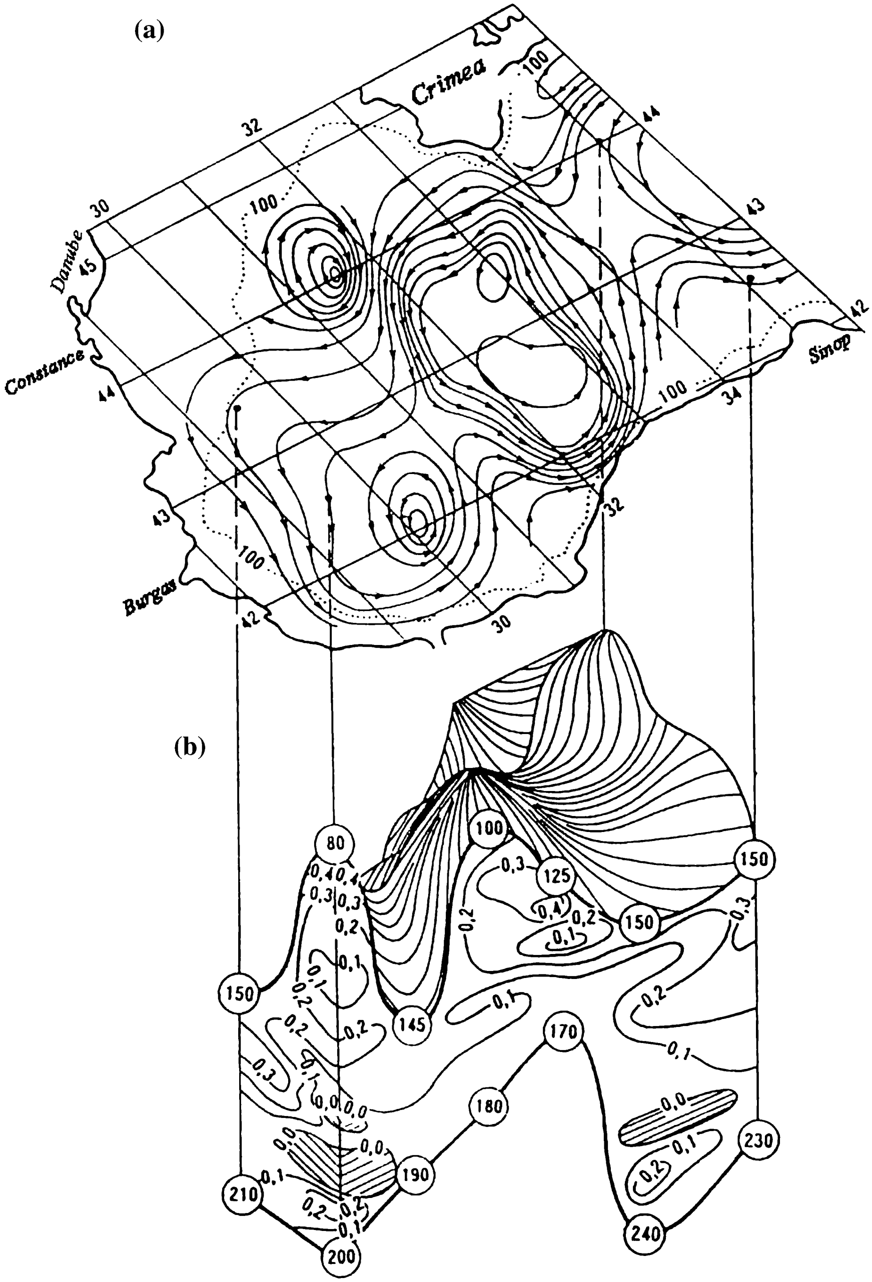


Fig. 3.11 Water circulation at depth of 50 m (**a**) and topography of the C-layer boundaries in axonometric projection (**b**) in July, 1983 in the western Black Sea (Fashchuk and Aizatulin 1986) (Isolines in the C-layer—oxygen concentrations, mL/L; figures on the C-layer boundaries—depths, m; hatching—lens with zero oxygen content)

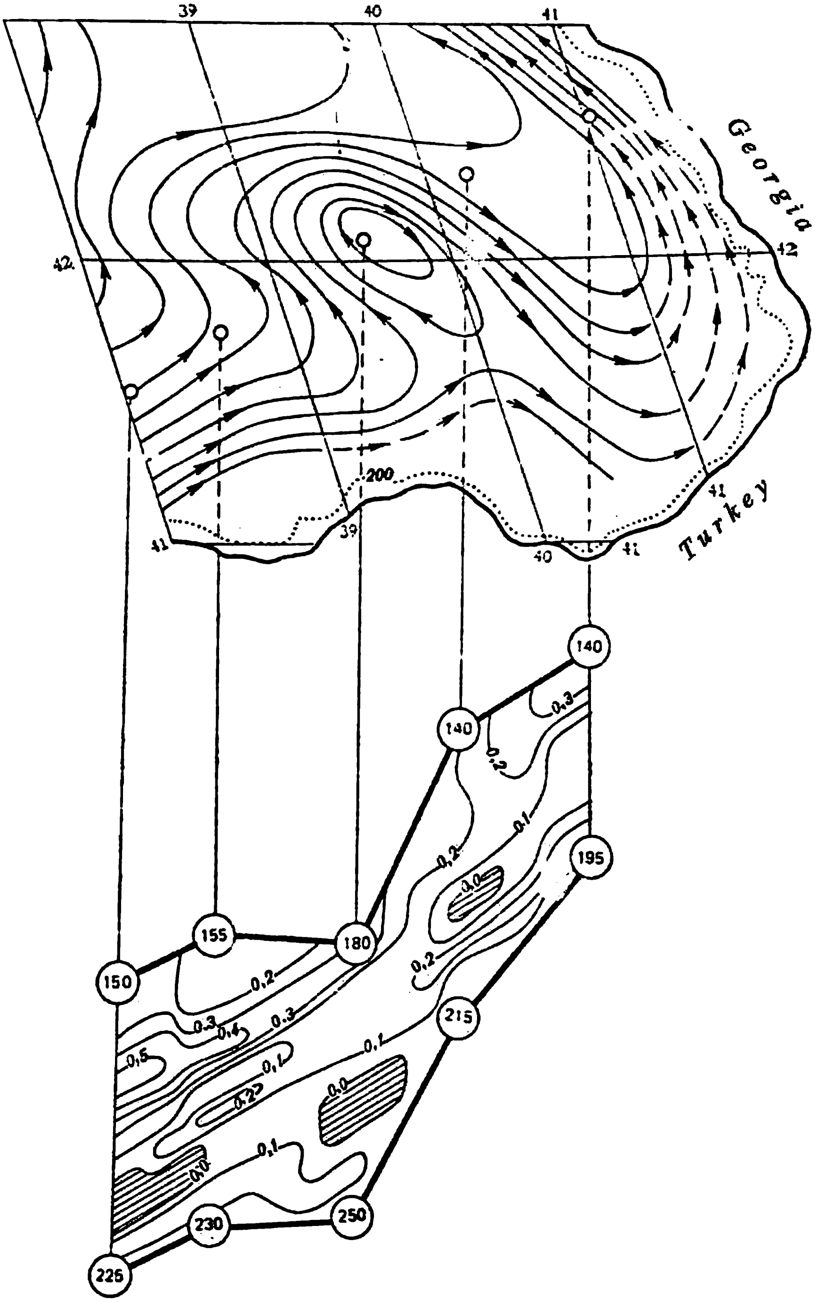


Fig. 3.12 Water circulation at depth of 50 m and cross-section of the C-layer in the eastern Black Sea in August, 1983 (Fashchuk and Aizatulin 1986) (explanatory notes as in Fig. 3.11)

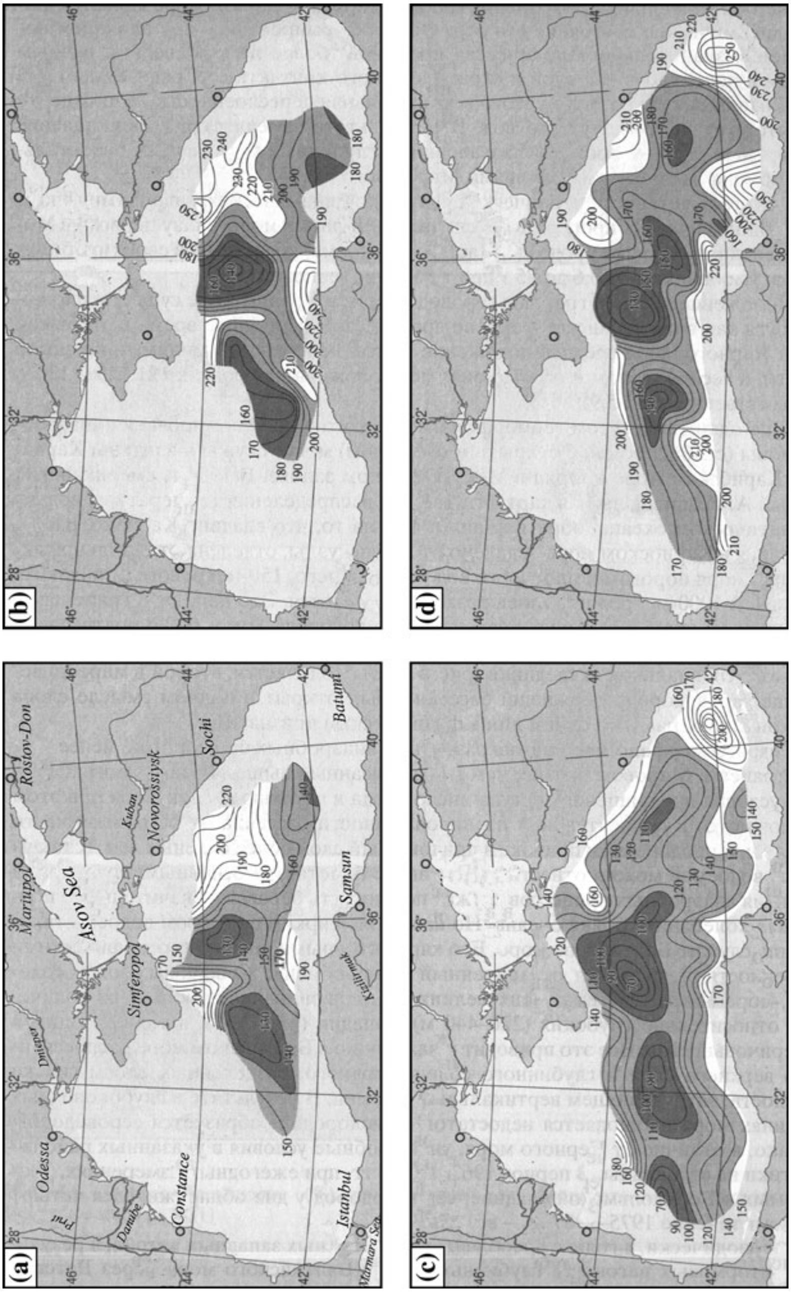


Fig. 3.13 Topography of the upper boundary of the C-layer in the Black Sea in 1984–1985 (Fashchuk 2002) (**a**, **b**, **c**, **d**—winter, spring, summer, autumn, respectively)

parallel determinations of hydrogen sulfide by volumetric (iodometric) and photometric methods. The latter, as it is known, allows determining microconcentrations of hydrogen sulfide in seawater without other reduced sulfur forms. For the control, in 46 cases the parallel determination of thiosulfates in the layer of the oxygen-hydrogen sulfide coexistence was carried out with use of the Kurtenaker–Vollack method.

Irrespective of station locations, in the whole depth range of the upper boundary of hydrogen sulfide the estimates of its position by independent methods coincided within their accuracy. Intermediate forms of sulfur oxidation in the coexistence zone were not found by either direct (thiosulfates) or indirect (by difference of hydrogen sulfide readings obtained with two methods) determinations. This difference appears only at the lower boundary of the C-layer zone. The experiment proved that *use of iodometric method for determination of position of the upper boundary of hydrogen sulfide could not lead to its overestimate due to methodical incorrectness* (Novoselov et al. 1987).

After elimination of doubts in correctness of the methodical approach used at determination of position of the upper boundary of hydrogen sulfide zone, we made conclusions about spatiotemporal (seasonal and synoptic) variability of its topography. Among them the main conclusions are as follows:

1. The upper boundary of the C-layer (H_2S-zone) represents the complicated wave-like surface which relief is determined by water circulation structure. The zone “breathes” in time with movement of synoptic eddy formations (SEF), and “depth” and “rhythm” of its breath coincide with the scales of temporal variability in their intensity and intensity of the Main Black Sea Current (MBSC). Such rings are capable of causing a local rise or deepening of the H_2S-zone in different areas of the sea by 50–80 m, independent on season (Fashchuk and Aizatulin 1986).
2. The depth of the upper boundary of hydrogen sulfide in the open sea may change by 65–70 m at a distance of 30 miles under the influence of SEF, and within a month (for the same reason)—by 30 m (Bryantsev et al. 1988a).
3. In the coastal zone (under the influence of upwelling) the C-layer position may change by 20–30 m within several days.
4. In the open sea the mean position of the upper boundary of hydrogen sulfide is the shallowest in winter (103 m), while in spring, summer and autumn it is located at depths of 121, 123, and 126 m, respectively (Table 3.3) (Fashchuk and Aizatulin 1986). According to other authors, in the 1980s these depths for the last three seasons were 124, 135 and 127 m (Bezborodov and Yeremeyev 1993).
5. The shallowest position of the upper boundary of the C-layer observed in the 1980s, was 50 m from the sea surface (in the centre of cyclonic circulation), its maximal deepening on periphery of the sea in the area of anticyclonic circulation off the Georgian coast reached 260 m.
6. At present, the fluctuations range of position of the hydrogen sulfide boundaries is 50–260 m, while half a century ago it did not exceed 110–160 m. The thickness of the C-layer on the average reaches 60–70 m, fluctuating from

Table 3.3 Seasonal characteristics (m) of topography of the C-layer boundaries at cross-sections from Yalta to Batumi (1) and from Sochi to Varna (2) in the Black Sea

Characteristic	Sect	Winter			Spring			Summer			Autumn		
		Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
H_{upper}	1	80	103	140	90	121	150	50	123	210	110	126	160
	2	100	106	120	100	115	140	110	129	150	90	115	160
H_{lower}	1	150	163	190	180	199	230	180	198	240	170	180	190
	2	170	175	190	150	178	220	180	192	210	170	181	210
ΔH	1		60			78			75			54	
	2		67			63			63			66	

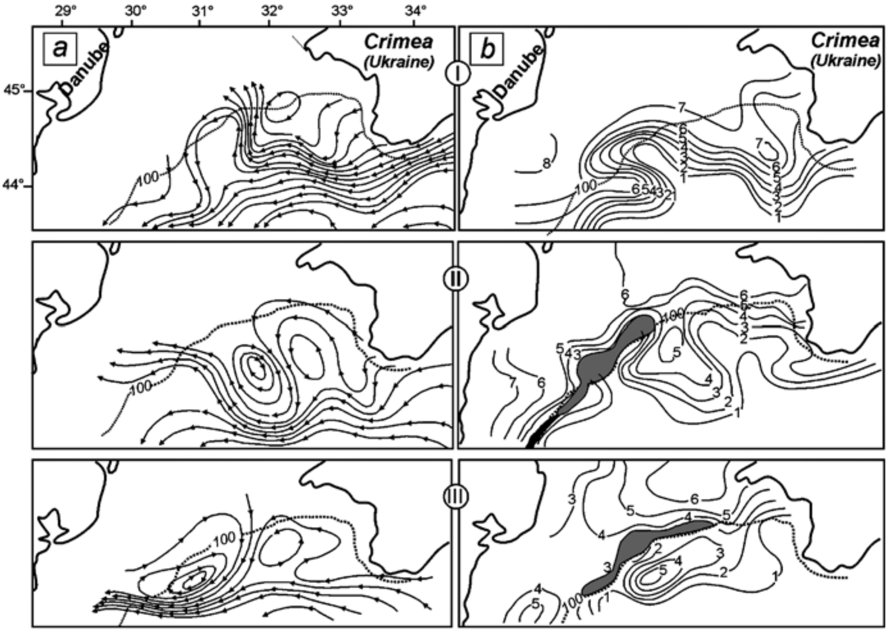


Fig. 3.14 Surface water circulation (**a**) and oxygen distribution (mL/L) at depth of 100 m (**b**) along the shelf edge of the northwestern Black Sea in 1986 (Fashchuk 1987) (*Black hatching*—zone of penetration of deep hypoxia onto the shelf)

30 to 150 m, and exceeds the data of 50 years ago in 1.5 times in winter, 10 times in spring, 4 times in summer, and 7 times in autumn (Fashchuk and Aizatulin 1986).

7. In the continental slope area of the northwestern Black Sea (70–100 m) on the periphery of anticyclonic synoptic eddies (zone of elevation of deep anaerobic waters) hypoxia can penetrate into the shelf zone to isobaths of 70–100 m (Fig. 3.14).
8. In the areas with shallow (90–100 m) position of the anaerobic zone upper boundary in the open Black Sea, associated with the centers of cyclonic

> circulations, the development of hypoxia ($O_2 < 1$–3 mL/L) in the photic layer (30–50 m), caused by oxygen consumption for oxidation of hydrogen sulfide imported there from the depths, is observed (Fashchuk and Aizatulin 1986; Fashchuk 2002). According to the mean long-term data (Shulgina 1961), during the spring season isooxigenes of 1 and 2 mL/L in the Black Sea should be located at depths of 100 and 80 m, respectively. In 1979 the isooxigene of 2 mL/L reached a depth of 50 m, while in 1981 the oxygen concentration at this depth was <1 mL/L (Fig. 3.15).

If one supposes that the maximal velocity of upward movement in the centre of quasistationary cyclonic circulation is 10^{-3} cm/s (Dzhiganshin et al. 1976), it would take more than 40 days for water elevation noted in 1979 and about 80 days for that in 1981.

3.3.2.3 Primary Causes of Seasonal Dynamics of Anaerobic Zone Boundary

During the field investigations of 1982–1986 many authors obtained strong evidence for the relationship between topography of the C-layer boundaries and the character of water circulation. Its position is actively affected by synoptic eddy formations and their displacements on the sea aquatory, intensity of large-scale elements of the Black Sea circulation—Main Black Sea Current (MBSC) and quasistationary cyclonic circulations (QCC) in the eastern and western parts of the sea, and offshore—inshore circulation.

(1) *Structure of water circulation*. In July–August, 1985 in the eastern Black Sea on the test site, which aquatory for many years is regularly crossed by the "Batumi" coastal anticyclonic eddy (see Fig. 3.12), we conducted two oceanographic surveys, fixing the evolution of this SEF in parallel with changes in topography of the C-layer boundaries (Fig. 3.16).

The qualitative relationship of the latter with the character of water circulation is obvious. In the center of cyclonic circulation (station 87) the hydrogen sulfide boundary rose up to 120 m, while on its periphery (stations 88, 91, 96) it was deepened down to 150–160 m. At the same time, in the center of anticyclonic eddy (station 92) the hydrogen sulfide boundary sank to 220 m, and on the periphery (stations 90, 93–95) it rose up to 160–180 m (Table 3.4). Within a month, with eddy transformation, the upper boundary of the C-layer rises by 30 m in its center. For the same time on the periphery of cyclonic circulation (stations 89, 97) it deepens by 30–50 m, while in the central part the boundary rises by 30 m.

Also, the position of the lower boundary of the C-layer varies synchronously with this surface. With that, its thickness in some cases changes in 2–3 times (stations 91, 93), its mean value, as well as average depths of the upper and lower boundaries of the layer, remains almost constant—47, 160, 210 m, respectively. This fact evidences that, when estimating the tendencies in interannual and

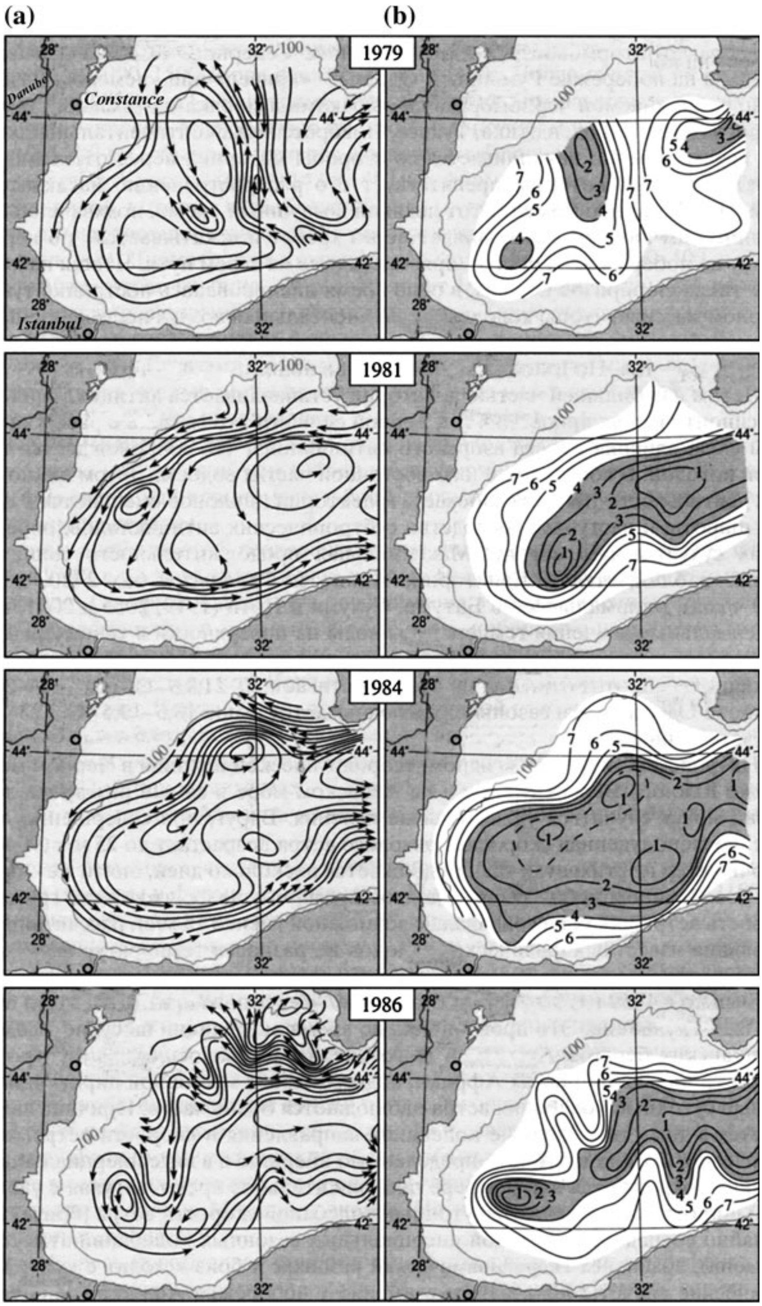


Fig. 3.15 Water circulation (**a**) and oxygen concentration, mL/L *(***b***)* at depth of 50 m in the western Black Sea (Fashchuk 2002)

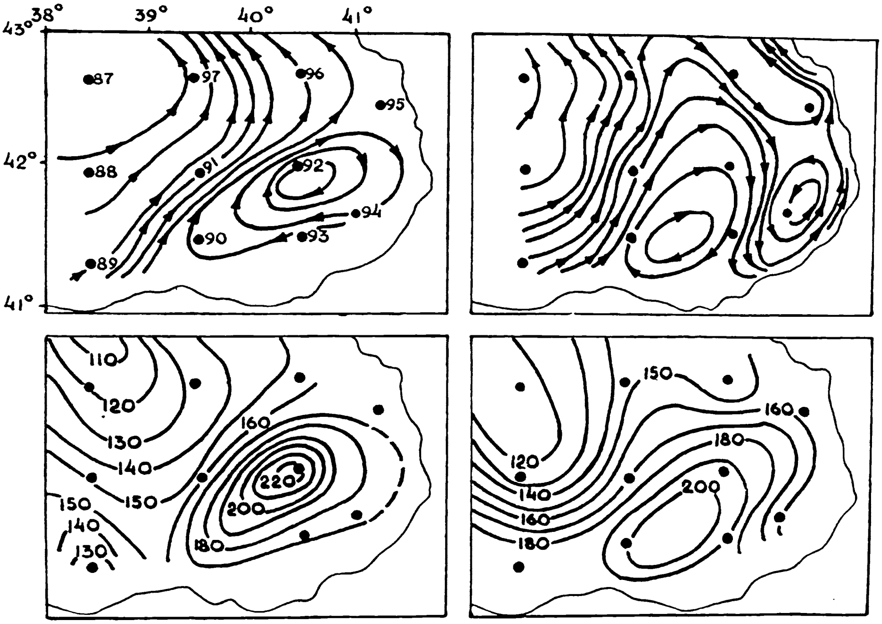


Fig. 3.16 Water circulation at depth of 50 m (*top*) and topography of the upper boundary of the C-layer, m (*bottom*) in the eastern Black Sea in July (*left*) and August (*right*), 1985 (Bryantsev et al. 1988a) (Figures near points—Nos. of st. from Table 3.4)

Table 3.4 Characteristics of the oxygen–hydrogen sulfide coexistence layer on the site in the eastern Black Sea in July and August, 1985 (Bryantsev et al. 1988a)

Station number	C-layer boundaries				Thickness of C-layer	
	Lower		Upper			
	July	August	July	August	July	August
87	120	120	160	160	40	40
88	150	120	180	160	30	40
89	130	180	180	220	50	40
90	180	200	220	240	40	40
91	150	160	170	220	20	60
92	220	190	260	240	40	50
93	170	190	250	220	80	30
94	180	160	240	220	60	60
95	170	160	210	210	40	50
96	150	150	210	200	60	50
97	130	160	170	220	40	60
Mean	159	162	205	210	47	47

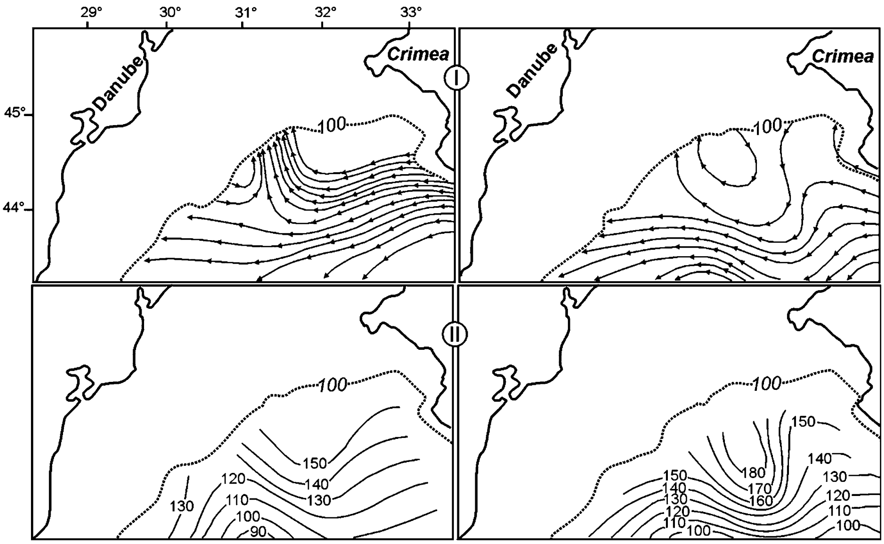


Fig. 3.17 Water circulation at depth of 100 m (I) and upper boundary of hydrogen sulfide, m (II), 20–24 May (*left*) and 27–31 July (*right*) 1985. (Fashchuk et al. 1987) (*Dashed line*—the 100-m isobath)

seasonal dynamics of the C-layer boundaries, it is necessary to use only space-averaged data.

We carried out the similar investigations (repeated surveys) (Fig. 3.17) in May–July, 1985 in the western Black Sea on the site which aquatory is regularly crossed the "Crimean" anticyclonic eddy (see Fig. 3.13). Outside its development zone, in the area of the Main Black Sea Current (Fig. 3.17, bottom), where water circulation maintained the quasistationary character, over almost 2 months the upper boundary of the C-layer remained at depths of 90–100 m. But in the eddy formation zone by the end of July the upper boundary of hydrogen sulfide in the center of the site sank from 150 to 180 m.

(2) *Synoptic situations and character of atmospheric transfers*. The intensity and character of the Black Sea water circulation depend significantly on the intensity and character of atmospheric transfer over its aquatory. Thus, numerical calculations (Moskalenko 1975) showed that steady winds of the northern quarter favored intensification of the cyclonic Main Black Sea Current and quasistationary cyclonic circulations in both parts of the sea. Winds of the southern quarter induce the anticyclonic circulation, resulting in lessening of the MBSC and QCC intensities.

After the analysis of synoptic situations preceding the oceanographic surveys in August and November, 1982, and direction of winds prevailing in these periods, it was possible to find out (Fashchuk and Aizatulin 1986) that the registered abnormal local rise (up to 50 m) of the upper boundary of hydrogen sulfide zone in August, 1982 (see Fig. 3.10,I) coincided with the uncharacteristic for summer

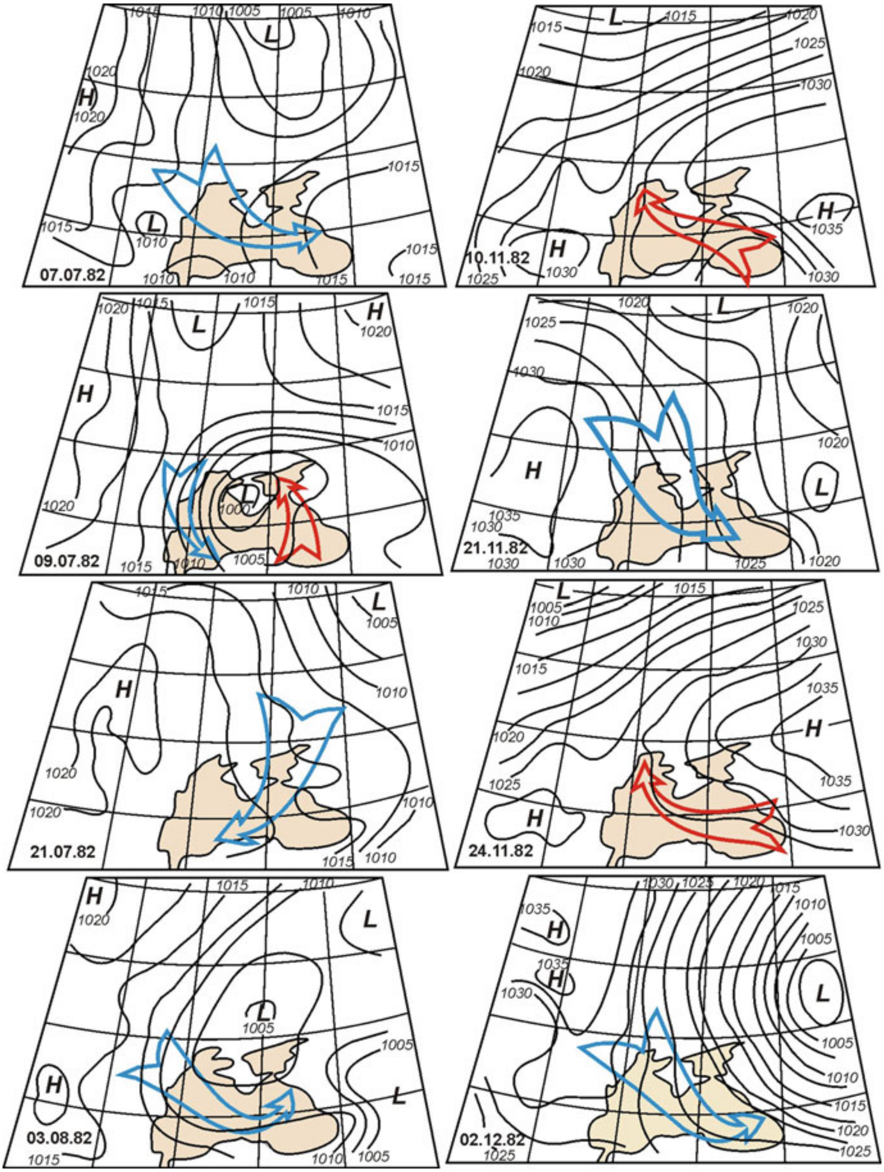


Fig. 3.18 Synoptic situations and prevailing atmospheric flows in summer (*left*) and autumn (*right*), 1982 (Fashchuk and Aizatulin 1986)

cyclonic activity over the sea aquatory. The anomalously continued (during a month) northern atmospheric flow (Fig. 3.18, left) resulted in strengthening of cyclonic circulation in the eastern Black Sea and, as consequence, intensive upwelling of deep water in the center of this area.

But in autumn the alternation of the northwestern and southeastern flows with an interval of 5–10 days (Fig. 3.18, right) prevented the development of intensive cyclonic circulation, and the upper boundary of the C-layer in this season remained at a rather stable level (see Fig. 3.10,II).

3.3.3 Microstructure of the O_2–H_2S Coexistence Layer and Possible Mechanisms of its Formation

Over the five-year (1982–1986) period of field investigations (see Sect. 3.3.2) we have collected the dataset on spatial characteristics and hydrochemical structure of the C-layer during the different seasons (Table 3.5). At the analysis of this information it emerged that the mean depths of the C-layer boundaries and, correspondingly, its thickness vary essentially from one season to another. For this reason, when superimposing the mean seasonal profiles of the characteristics constructed in one scale, their end points do not coincide that makes a comparison difficult.

To solve this problem, when constructing the graphs of vertical distribution of oxygen, hydrogen sulfide, and oxidation rate of the latter in the C-layer during

Table 3.5 Mean seasonal characteristics of the C-layer in the Black Sea (Fashchuk et al. 1990)

Depth (m)	Oxygen (mL/L)				Hydrogen sulfide (mL/L)				Rate of H_2S oxidation (gH_2S/m^2 day^{-1})			
	Spr.	Sum.	Aut.	Win.	Spr.	Sum.	Aut.	Win.	Spr.	Sum.	Aut.	Win.
70		0.15				0.04				1.0		
80		0.14				0.05				1.2		
90		0.23	0.29	0.26		0.04	0.13	0.08		2.3	6.1	2.5
100	0.32	0.16	0.26	0.18	0.13	0.11	0.16	0.15	6.0	2.3	6.8	4.1
110	0.23	0.13	0.22	0.19	0.11	0.11	0.15	0.16	3.6	2.3	5.4	4.9
120	0.21	0.19	0.23	0.22	0.16	0.13	0.13	0.18	4.9	4.5	4.7	5.1
130	0.21	0.19	0.21	0.23	0.21	0.16	0.18	0.23	6.1	4.0	5.9	6.2
140	0.18	0.19	0.17	0.15	0.25	0.23	0.22	0.28	7.1	6.3	6.0	5.2
150	0.17	0.15	0.14	0.17	0.26	0.27	0.25	0.31	6.7	6.0	5.5	6.6
160	0.14	0.13	0.12	0.14	0.30	0.26	0.28	0.39	6.2	5.1	4.6	7.5
170	0.15	0.15	0.10	0.12	0.35	0.23	0.38	0.38	7.6	5.2	5.5	6.7
180	0.14	0.14	0.11	0.15	0.31	0.29	0.34	0.35	6.2	5.9	5.7	8.7
190	0.10	0.13	0.15	0.09	0.37	0.29	0.25	0.44	5.2	5.7	5.6	6.5
200	0.11	0.14	0.07		0.47	0.30	0.33		7.0	5.1	3.7	
210	0.16	0.15			0.37	0.34			7.1	8.0		
220	0.26	0.13			0.42	0.26			11.9	4.6		
230	0.48	0.19			0.31	0.32			24.6	7.6		
240	0.45	0.27			0.47	0.28			35.0	12.5		
250	0.05	0.18			0.68	0.42			5.6	12.5		
Mean	0.21	0.17	0.17	0.17	0.32	0.22	0.23	0.27	9.4	5.4	5.5	5.7

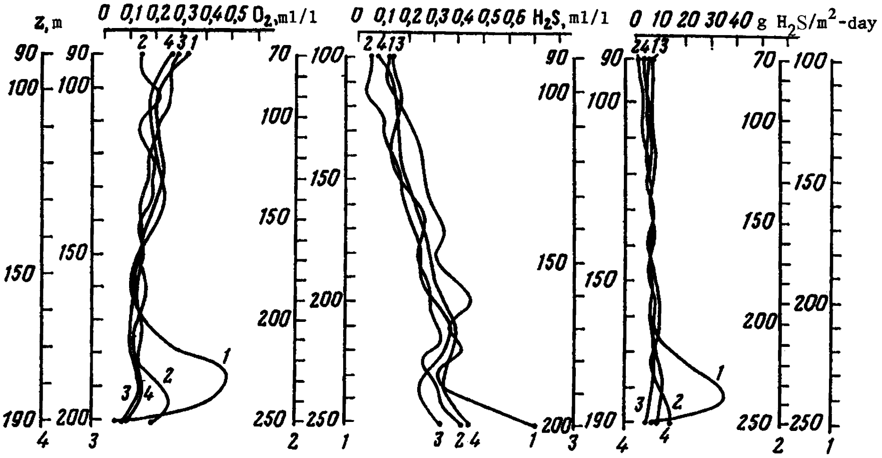


Fig. 3.19 Mean seasonal profiles (from left to right): oxygen, hydrogen sulfide, its oxidation rate in the C-layer (Fashchuk et al. 1990) (1, 2, 3, 4—spring, summer, autumn, winter, respectively)

Table 3.6 Frequency of occurrence (%) of oxygen and hydrogen sulfide concentrations in the C-layer for the 1982–1986 period

Concentrations (mL/L)	Oxygen				Hydrogen sulfide			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
0.00–0.10	37	47	34	35	22	25	32	28
0.11–0.20	32	30	36	34	18	20	17	15
0.21–0.30	20	13	23	16	20	20	18	16
0.31–0.40	6	6	5	10	17	15	12	15
0.41–0.50	4	3	1.7	3	10	10	12	15
0.51–0.60	1	0.7	0.3		8	5	3	9
0.61–0.70		0.1		2	3	3	4	1
0.71–0.80		0.1			2	1	1	1
0.81–0.90		0.1				0.5	0.5	
0.91–1.00								
1.01–1.10						0.5		
Number of observations	326	885	326	68	325	882	324	68

various seasons the different depth scales have been used. This allowed identifying the profiles for all seasons and making their comparison (Fig. 3.19).

3.3.3.1 Oxygen

The statistical analysis of dataset on oxygen concentrations in the C-layer showed that (Table 3.6) (Fashchuk et al. 1990):

- almost in all seasons their range there was 0.03–0.90 mL/L;
- mean oxygen concentrations in the C-layer essentially coincided in summer, autumn, and winter (0.17 mL/L) but in spring they increased to 0.21 mL/L; with that, the variance value is constant in all seasons;
- range of O_2 concentrations in the C-layer was 0.03–0.6 mL/L; with that, on the average for a year their values of 0.03–0.2 mL/L were noted in 70%, and those of 0.3–0.6 mL/L—in 10% of cases;
- maximal O_2 concentrations (0.61–0.9 mL/L) were fixed only in isolated cases (especially, during the spring-summer period, when the lower boundary was maximally deepened) at the lower boundary of the C-layer (see Fig. 3.19) that was confirmed by the data of other authors, obtained in the 6th cruise of R/V *Vityaz* (April–May, 1984) (Lukashev 1987);
- in the autumn–winter season the variability of oxygen concentrations in the C-layer was much lower than during the spring-summer period.

3.3.3.2 Hydrogen Sulfide

The hydrogen sulfide concentrations in the C-layer range from 0.03 to 0.86 mL/L. Herewith, their mean summer, autumn, winter, and spring values are 0.22, 0.23, 0.27, and 0.32 mL/L, respectively;

- despite the layer-averaged concentrations in winter and spring are somewhat higher than in other seasons (see Table 3.3), their variance does not change with season, as is the case with oxygen;
- mean annual occurrence of concentrations from 0.03 to 0.3 mL/L is 62%, 0.32–0.5 mL/L—27%, 0.51–0.7 mL/L—9%, and a share of maximal concentrations of 0.71–0.86 mL/L constitutes 2–3%. The C-layer is characterized by presence of lens with zero values of reacting components (Figs. 3.11–3.12).

In distinction from the previous years, in all seasons of the 1982–1986 period the non-uniform vertical distribution of both oxygen and hydrogen sulfide was a typical feature, independent on sea area. Earlier, it had a monotonous character (Aizatulin and Skopintsev 1974). Obviously, these qualitative changes in the C-layer microstructure may be associated with intensive dynamic processes occurring now in the zone of hydrogen sulfide oxidation under the influence of complicated eddy structure of water circulation. In the upwelling areas the hydrogen sulfide flux into the C-layer is intensified. As a result, its thickness increases to 150 m (see Fig. 3.10).

3.3.3.3 Rates of Hydrogen Sulfide Oxidation

The fluctuations range of rates of hydrogen sulfide oxidation in the C-layer is 0.00–0.35 g H_2S/m^2 per day. Herewith:

- in all seasons, except for winter, a share of values to 0.1 g per day is 80–90%, with an increase in winter up to 97%;
- the sea-averaged integral rate of hydrogen sulfide oxidation in the C-layer varies from 0.7 in winter to 1.1 kg H_2S/m^2 per year in summer that is 5–6 times over the estimates made in the 1970s and 40 times higher than the estimates of hydrogen sulfide production (Skopintsev 1975);
- in the upwelling zones (see Fig. 3.10,I) rates of hydrogen sulfide oxidation increase sharply (2–3 times), their vertical profiles take the complicated form, and the layer-integrated rate in these cases may reach 6 g H_2S/m^2 per day;
- depending on a character of water circulation, several centers of intensive hydrogen sulfide oxidation can exist simultaneously (Fig. 3.20).

The estimations of rate of hydrogen sulfide oxidation in the contact zone with oxygen, made by various methods (Sorokin 1970; Deuser 1970; Belyaev 1974; Aizatulin and Skopintsev 1974), almost coincide (on the average 130 g H_2S/m^2 per year) and several times, as is the case with our data, exceed the known determinations of rate of its formation (25 g H_2S/m^2 per year) (Skopintsev 1975), occurring in the top (3–5 cm) layer of sediments and at the interface between aerobic and anaerobic zones. Thus, *the balance for hydrogen sulfide in the Black Sea has not been obtained until recently.*

3.3.4 Seasonal Statistical Portraits of the C-Layer and Possible Mechanisms of its Microstructure Formation

To estimate the possible causes of formation and variability of the C-layer microstructure and rates of hydrogen sulfide oxidation, we have used the apparatus of mathematical statistics. The matter is that owing to large spatial variability of topography of the C-layer boundaries, the number of effective observations (cases of simultaneous presence of oxygen and hydrogen sulfide in water sample) in the upper and lower parts of the layer during all seasons was much smaller than in its central part (Table 3.6). In this connection, to solve the posed problem correctly we used F-test representing the ratio of the squares of variances of series with different number of observations. Its actual value was compared with the critical value (F_{cr}) for the 95% significance level, given in the standard tables (Urbakh 1975). The results of comparison were written in matrix cells (Fig. 3.21). In the matrix, a white cell denotes that series belong to the same general population ($F < F_{cr}$), and black cell means that they are relative to different populations ($F > F_{cr}$).

Thus, by sequential comparison of samples of average values of oxygen, hydrogen sulfide, and rates of oxidation of the latter (r_s) at the observation depths in the C-layer (5 m apart) with series of these characteristics at greater depths, we composed the *statistical portraits* of seasonal variability of their profiles. In case the series at different depths belong to the same sample the fluctuations in their elements are determined by a common cause, or the combined effect of various contributing factors at the depths compared is the same. In other case

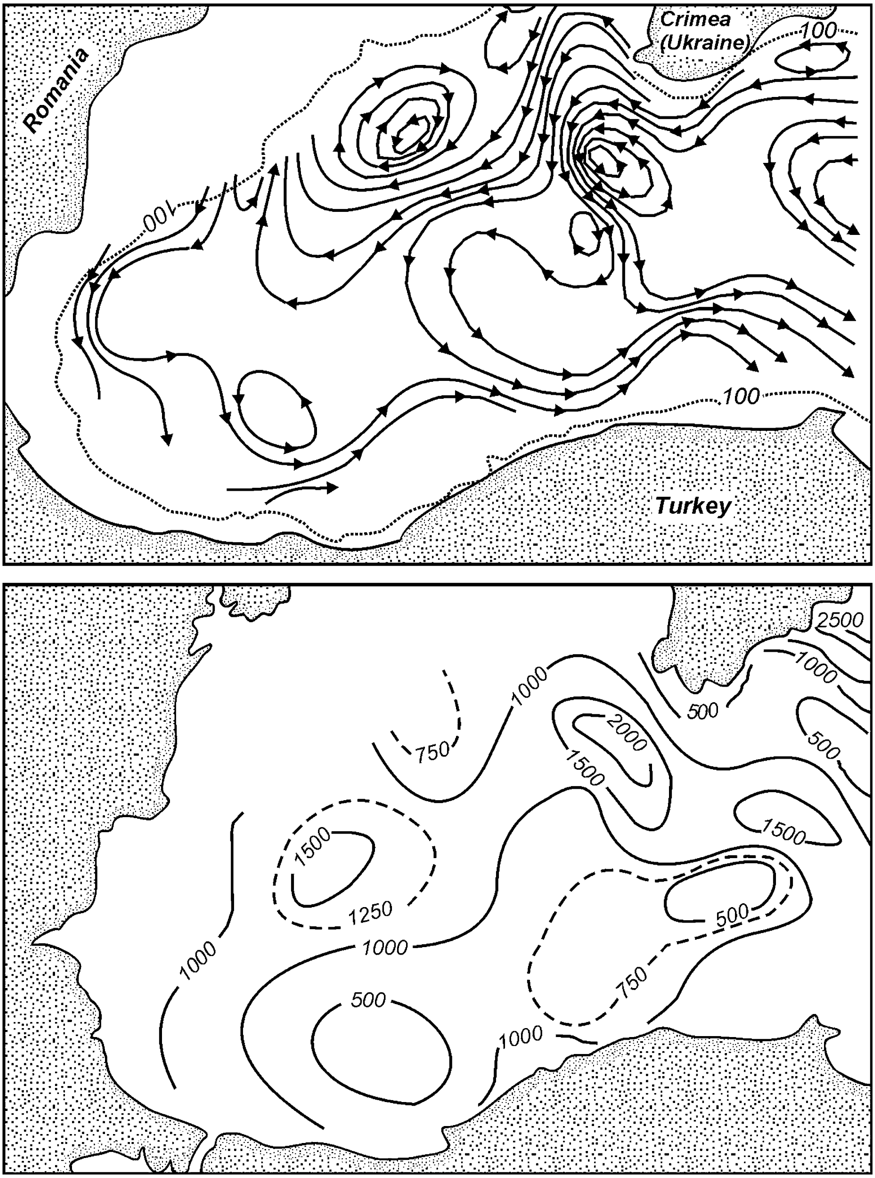


Fig. 3.20 Water circulation at depth of 75 m (*top*) and distribution (bottom) of integral rate of hydrogen sulfide oxidation Rs (g m^{-2} per year) in the C-layer of the western Black Sea in July 1983 (Fashchuk et al. 1987)

(samples belong to different general populations), the changes in their elements are governed by different causes, or the resulting contribution of the sum of the factors to this process is different for each of the depths that are compared.

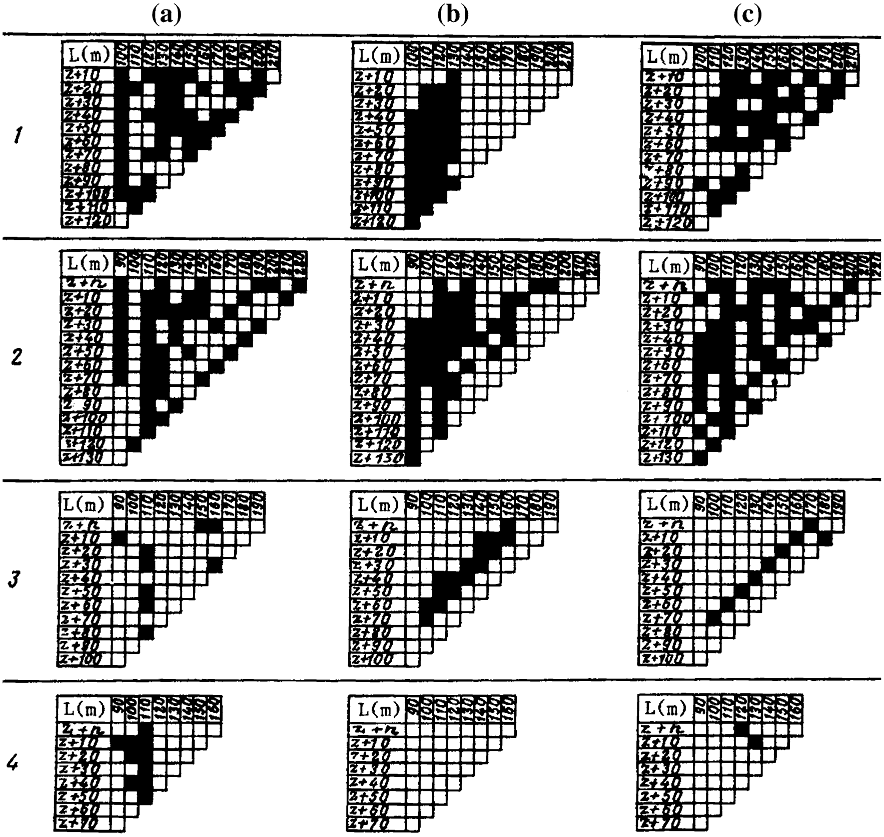


Fig. 3.21 Statistical portraits of seasonal variability of hydrochemical characteristics in the C-layer of the Black Sea (Fashchuk et al. 1990) (**a**, **b**, **c**—oxygen, hydrogen sulfide, and rate of hydrogen sulfide oxidation, respectively; *1*, *2*, *3*, *4*—spring, summer, autumn, winter, respectively)

3.3.4.1 Oxygen

The statistical portrait of oxygen concentration variability in the C-layer evidences that during the spring–summer period (Fig. 3.21a, 1, 2) variations of this parameter are more heterogeneous than in the autumn–winter season (Fig. 3.21a, 3, 4), when in the most part of the layer the O_2 concentrations belong to one general population. The exceptions are the depths of 100–110 m, at which the oxygen pulsations developing in autumn and amplifying by winter have different character than in the rest of the layer.

It is difficult to explain a variety of vertical fluctuations of the investigated characteristic during the spring–summer season only by heterogeneous intensity of life activity of microorganisms, as our colleagues think (Lukashev 1987). The hydrodynamic instability of deep currents and conditions of vertical exchange, amplifying in this period due to the known lessening of cyclonic circulation intensity in the Black Sea and formation of seasonal thermocline, is more probable reason of this phenomenon (Fashchuk et al. 1990).

During the autumn -winter period the fluctuations of oxygen concentrations in the C-layer become more homogeneous, because the intensity and stability of cyclonic circulations at this time strengthen, regime of advection in the deep layers is normalized, and development of convective mixing, in turn, stabilizes conditions of a vertical exchange. The anomalies at depths of 100–110 m may be caused by biochemical mechanisms that requires experimental test.

3.3.4.2 Hydrogen Sulfide

Despite the similarity of seasonal profiles of hydrogen sulfide (see Fig. 3.19), the statistical portraits of its variability essentially differ (Fig. 3.21b), the character of these dissimilarities being somewhat different than for oxygen (Fashchuk et al. 1990). Instead of chaotic fluctuations in the whole layer, typical for oxygen during the spring–summer period, the character of hydrogen sulfide fluctuations during these seasons vary clearly between two layers: from 90–100 to 120 m and from 150 to 230 m (Fig. 3.21b, 1, 2). In spring the distinction between layers is more pronounced, while in summer, despite the remaining two-layer structure on a scale of the whole coexistence zone, the type of fluctuations at depths of 180–190 m changes.

The reason of such separation may be that in spring in the upper C-layer the H_2S concentrations are formed mainly under the influence of biochemical processes determining its oxidation, while in its lower part the dynamic factors—three-dimensional advection and diffusion, are more effective. By the summer, when intensity of dynamic processes supplying the C-layer with hydrogen sulfide decreases, the microbiological mechanism starts to manifest itself effectively in deeper water (180–190 m).

In autumn the two-layer character of hydrogen sulfide fluctuations breaks and by winter the whole field of H_2S concentration values represents one universe—mechanisms of formation of its structure are common in the whole layer (Fig. 3.21b, 3, 4). The most probable cause of this transformation may be associated with autumnal intensification of physicodynamical mechanisms of convective mixing and vertical turbulent exchange which by winter suppress almost completely the effect of the microbiological factor.

3.3.4.3 Rates of Hydrogen Sulfide Oxidation

The statistical portraits of this characteristic of the C-layer, derivative of the O_2 and H_2S concentration values, have essential seasonal differences (Fig. 3.21c). The spring-summer season is characterized by randomness of its fluctuations in the whole layer, similar to oxygen portrait, while during the autumn -winter period the portrait of its variability corresponds completely to the hydrogen sulfide portrait. Thus, the variability in intensity of hydrogen sulfide oxidation during the spring–summer season is better determined by mechanisms and regime of the C-layer supply with oxygen, while in the autumn–winter period—with hydrogen sulfide.

3.4 Interannual Dynamics of the H_2S-Zone Boundary

Now it does not seem possible to make a certain conclusion about the interannual variability of position of the hydrogen sulfide upper boundary in the Black Sea because of a lack of the system of regular observations on the unified methodical basis. Nevertheless, the existence of hydrogen sulfide in the Black Sea is determined first of all by a complex of specific physicodynamical conditions preventing the penetration of oxygen into its deep layers. Thereupon, the hypothesis that the topography of the H_2S-zone boundary in the Black Sea (H_s) was associated with topography of its characteristic physical surfaces, has been suggested (Bryantsev et al. 1988b).

3.4.1 *Characteristic Physical Surfaces of the Black Sea*

In summer, the water column of the Black Sea is subdivided into some layers with different physical characteristics, boundaries between which serve as

Photo 3.4 Participants of the 44th cruise of R/V *Dmitry Mendeleev* in the Black Sea, summer 1989

Photo 3.5 The Black Sea. The 44th cruise of R/V *Dmitry Mendeleev*, August 1989

boundaries of life concentration for various phyto- and zooplankton forms and pelagic commercial hydrobionts at early stages of development (Fig. 3.22). They include:

1. Warm upper mixed layer (UML), lower boundary of which usually coincides with depth of the 20°C-isoterm.
2. Layer of seasonal thermocline, or maximal temperature gradient (STL).
3. Cold intermediate layer (CIL), lower and upper boundaries of which coincide with depth of the 8°C-isotherm.
4. Layer of maximal salinity gradient, or permanent halocline (PH), upper boundary of which (H_{gs}) coincides with depth of the 18.6‰-isohaline.
5. Layer of maximal density gradient, or main pycnocline (MP), lower and upper boundaries of which ($H_{g\rho}$) coincide with position of vertical density gradient equal to 0.03 σ_t units.
6. The main body of deep Black Sea water with temperature of 9°C, salinity of 22.3‰, and density of 17.22 σ_t units lies below the MP-layer (Project "The Seas … 1991a, b).

In winter, in the process of convective mixing the lower boundary of the UML deepens to the depth of occurrence of the upper boundary of permanent halocline, the seasonal thermocline disappears, the upper boundary of the CIL outcrops, and water column attains a three-layer structure consisting of the upper mixed layer, layer of permanent halocline (almost coinciding with the MP position), and main deep water mass (Ovchinnikov and Popov 1987; Ovchinnikov et al. 1991).

3.4.1.1 Permanent Halocline and Main Pycnocline

The biologically active upper and anaerobic deep layers are separated by permanent halocline which depth of core (layer of the maximum salinity gradients) coincides with position of layer of the maximal density gradient in the permanent

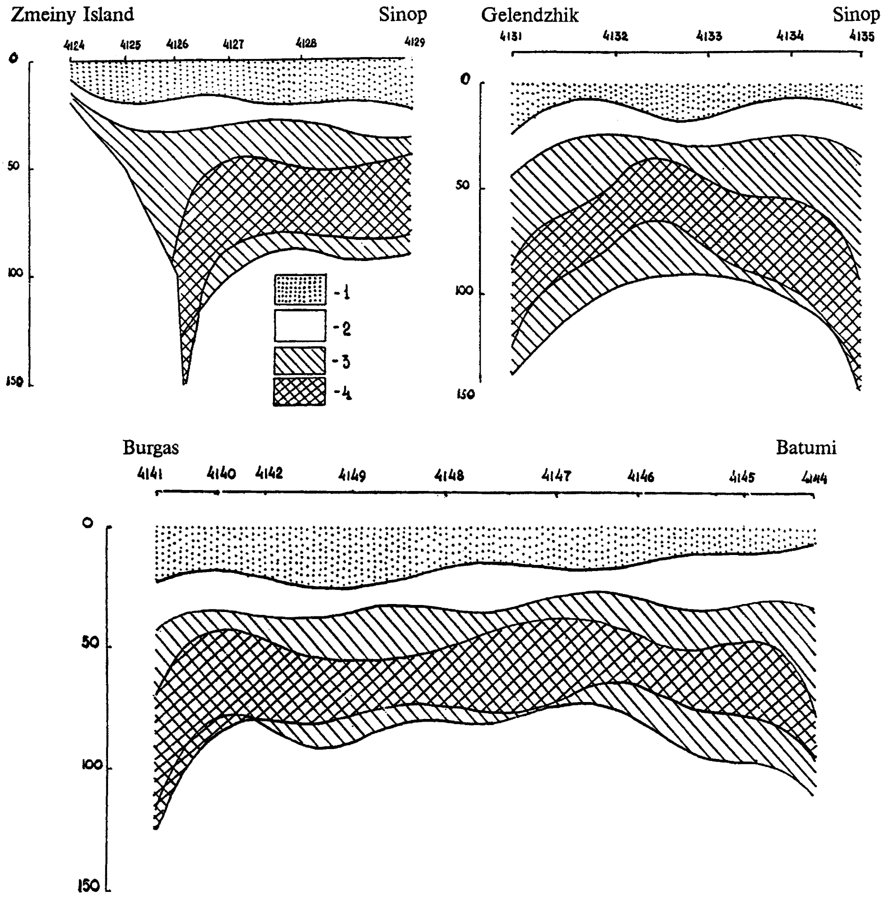


Fig. 3.22 Topography of boundaries of the characteristic physical surfaces at sections in the Black Sea in summer, 1989 (the 44th cruise of R/V *Dmitry Mendeleev*—Photo 3.4–3.5): (*1* upper mixed layer, UML; *2* seasonal thermocline, STL; *3* cold intermediate layer, CIL; *4* main pycnocline, MP)

pycnocline. Its origin is associated with the above-mentioned features of the Black Sea exchange with the open aquatories of the World Ocean and parallel inflow of considerable volume of fresh river runoff. *Ecologically*, the presence of permanent halocline in the Black Sea was a primary cause of generation and centuries-long maintenance of anaerobic conditions in its deep layers and, correspondingly, filling of more than 90% of its volume with bacterial forms of life only. Moreover, the PH plays also an important role in vertical distribution of hydrobionts in biologically active aerobic layer (Vinogradov et al. 1992). The characteristic features of the surfaces under consideration are the following (Blatov et al. 1984):

- independent on season, depth of the core, upper and lower boundaries of the PH coincide with position of isohalines of 19.5, 18.6, and 20.0‰, respectively;

- depth of the PH core in the coastal zone is determined by processes of the autumn–winter mixing, and in the open sea—by intensity of the general water circulation (Fig. 3.23, top);
- in the western cyclonic circulation the range of seasonal variations of the PH boundaries position is higher than in the eastern one but even there it is 3 times smaller than on the periphery of the sea;
- values of vertical salinity gradients in the PH core in the periods of its extreme position are (200-500) × 10^{-4}‰/m;
- during the periods of the extreme PH position (Fig. 3.23, bottom) forms of the permanent halocline surface (maximal salinity gradient) and the H_2S boundary almost coincide and are determined by character of water circulation in these seasons;
- in the centers of cyclonic circulations of the open sea the minimal depth of tops of the PH domes is noted in March–April (to 22 m), and maximal—in the late autumn;
- the maximal long-term deepening of the PH on the basin periphery is registered in February–March (125–150 m), and minimal—in November–December (75 m), the maximums reaching 200 m in some years;
- in the open sea the maximal sharpening (by value of horizontal salinity gradients) of dome-like form of the PH is observed in April, and minimal—in October;

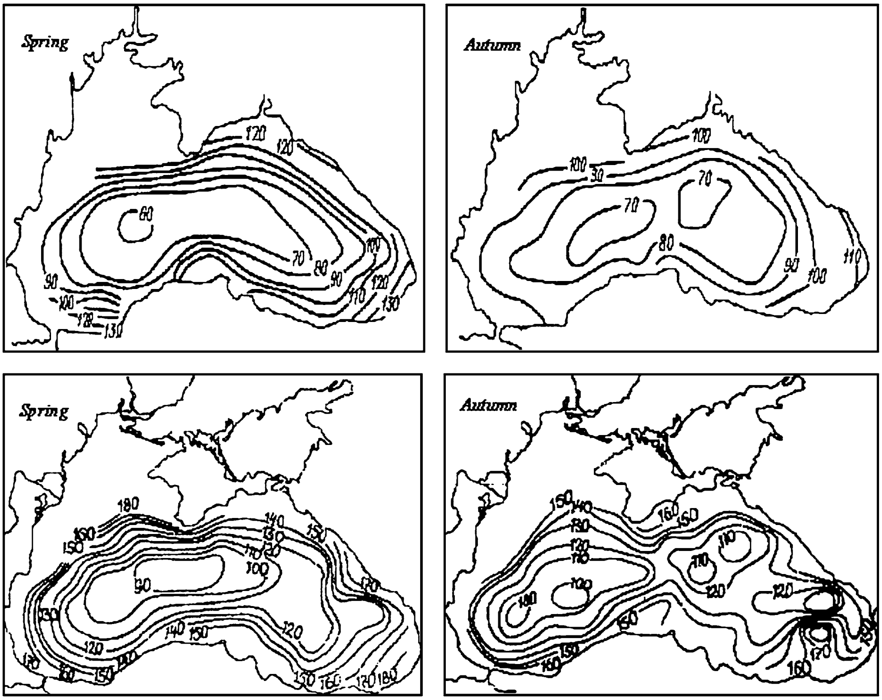


Fig. 3.23 Mean long-term (1960–1982) distribution of depth (m) of permanent halocline—layer of maximal salinity gradient (*top*) (Project "The Seas… 1991a, b), and position (m) of the H_2S-zone boundary (*bottom*) in individual seasons (Bezborodov and Yeremeyev 1993)

- because the Black Sea belongs to the category of basins, for which the river runoff is much lower than critical (by proportion to the sea volume), the climatic and anthropogenic changes in freshwater discharge and variations in volume transport of the Lower Bosporus Current do not affect significantly the position of the PH core;
- in summer the position of the upper and lower boundaries of the main pycnocline falls into the depth range of the CIL boundaries (Fig. 3.22);
- thickness of the MP layer increases (up to 50 m) in downwelling zones and decreases (to 5–10 m) in the centers of upwelling.

3.4.1.2 Cold Intermediate Layer

The presence of cold-water layer at intermediate depths (50–75 m) is an ecologically important feature of hydrological structure of the Black Sea. Till the 1950s there was an opinion (Knipovich 1930) that this phenomenon represented the remainder of the upper mixed layer persisting at the lower boundary of winter convection and renewing in winter under the influence of this mechanism on the whole aquatory of the sea. Under the further development of “convention” theory of the CIL formation (Kolesnikov 1953; Filipov 1968; Blatov et al. 1984), the areas of cold water formation (zones of maximum winter convection—the northwestern sea) and mechanisms of their transport above the main pycnocline layer (general circulation) around the basin aquatory were specified.

Nevertheless, the propositions of both “convention” and “advection and convection” theories in many cases did not agree with the results of field observations on parameters and character of the CIL distribution in the sea that occasioned the development of the present “climatic and oceanological” theory of its origin (Ovchinnikov and Popov 1987) proved to be much more adequate in comparison with the previous theories. Its main statements are the following:

- in winter, the homogenous active layer extending down to the upper boundary of the main pycnocline is formed on the whole sea aquatory, as a result of convective mixing;
- in the centers of cyclonic circulations density of this layer is maximal because pycnocline is elevated there to depths of 30–40 m, and heat, in the process of surface water cooling, is extracted from the thinner layer;
- as a result, at margins of the main pycnocline domes the downward density currents of supercooled surface water are formed;
- getting involved in the main cyclonic circulation, these waters, in the following, are spread over the whole deep sea, reaching the depth of 100 m and deeper near the continental slope;
- the CIL thickness in upwelling zones (centers of cyclonic circulations) is minimal, and on the periphery of the sea and sites with anticyclonic eddying it is maximal, its increase occurring due to deepening of the CIL lower boundary (involvement of permanent halocline in the area with intensified turbulence).

The statistical analysis of characteristics of the CIL showed the following (Gertman 1986; Altman et al. 1988):

- the proportion of deep and sunken supercooled surface waters in the layer is 1:5, and the mean long-term volume of its waters in winter, spring, summer, and autumn reaches 20.52; 20.95; 19.60, and 18.88 km^3, respectively;
- in the centers of cyclonic circulations up to 3,000 km^3 of water per year is transported from the deep sea into the photic layer due to upward motions, at mean velocity of $0.95\ 10^{-4}$ cm/s;
- minimal temperature in the CIL can reach 4.75–5.00°C, and the mean-long-term values of temperature, salinity, and density, dependent on season, are 7.79–8.00°C, 19.24–19.27‰, and 14.95–14.99, respectively;
- depth of the lower boundary of the CIL (by isohaline of 20‰) ranges from 75–80 m in the center of the sea to 125–150 m on its periphery.

It is the CIL that should be remembered with "a non-wicked quiet word" by thousands of people resting on the Crimean coast, when in the summer at the beaches of Yalta after offshore winds the water temperature within a few hours drops from 22 to 10–12°C—deep waters outcrop and remain there up to 6 days. At the end of the XX century this phenomenon episodically noted at the Black Sea coast of the USSR from the beginning of instrumental observations on water temperature (Bogdanova 1959), has begun to be observed almost annually (see further Sect. 3.7).

3.4.2 Relationship of the Cold Intermediate Layer Topography with Position of the H_2S-Zone Upper Boundary

As it was mentioned earlier, in the absence of regular long-term observations on the position of the H_2S-zone boundary in the Black Sea there is no possibility now to investigate a character of its interannual variability by data of direct measurements. At the same time, the bank of hydrological observations in the Black Sea allows constructing the continuous long-term time series of temperature and salinity for assessment of interannual variability of topography of boundaries of the characteristic physical surfaces of the basin, related genetically to the C-layer topography. Formalization of the relationship, for example, between the hydrogen sulfide boundary and position of the CIL boundaries enables to calculate its topography retrospectively by hydrological data.

3.4.2.1 Field Experiments

During the 44th cruise of R/V *Mikhail Lomonosov* (June 1985) on 56 stations of the survey covered the whole sea aquatory we fixed temperature and salinity by the Istok-4 probe with a vertical spacing of 10 m for calculation of the depths of the main pycnocline ($H_{g\rho}$) and upper boundary of the CIL (H_8). In parallel, with the same discreteness on 43 stations we determined the depth of the H_2S-zone boundary (H_s). The water samples for hydrochemical analyses of the hydrogen sulfide concentrations were taken with a cassette of plastic bottles of the MGI-4102 complex and 5-L Van Dorn viniplast bottles.

The position of the hydrogen sulfide zone boundary depends on conditions of vertical turbulent oxygen exchange which criterion is the Richardson static number (Ri), representing the ratio of vertical water density gradient to the square of vertical gradient (shear) of current velocities. Physically, this indicator counts the water stratification conditions and their dynamics, reflecting the ratio of energy flux rate into the deep layers to the rate of its transformation. The critical value of Ri (at which the oxygen exchange between water layers ceases) for the Black Sea is about 10 (Bryantsev 1981).

Thereupon, during June experiment at each station the direction and velocity of currents were measured above and below the main pycnocline (depths of 50 and 75 m), with the subsequent calculation of the criterion of intensity of vertical oxygen exchange Ri (Bryantsev et al. 1988b). The results of calculations of physical surfaces topography, boundary of the hydrogen sulfide zone, and conditions of vertical oxygen exchange are presented in Table 3.7.

Table 3.7 Depths of the main pycnocline ($H_{g\rho}$), upper boundary of the cold intermediate layer (H_8), H_2S-zone boundary (H_s) and criterion of oxygen exchange intensity in the halocline (Ri) in June, 1985

St.No.	$H_{g\rho}$	H_8	H_s	Ri	St.No.	$H_{g\rho}$	H_8	H_s	Ri
1	70	78	110	–	23	110	122	170	18
2	50	53	110	6	24	140	139	180	4
3	40	39	90	28	25	130	123	170	3
4	40	38	70	7	26	100	111	150	3
5	–	–	90	9	27	70	69	130	60
6	60	63	120	20	28	60	67	110	168
7	60	64	120	16	29	70	76	110	135
8	70	88	130	20	30	70	77	130	517
9	120	118	170	7	31	70	72	120	5
10	110	105	120	8	32	70	73	140	15
11	80	82	130	11	33	50	52	100	12
12	100	109	160	–	34	60	69	120	34
13	–	–	120	–	35	110	118	160	5
14	70	76	130	6	36	100	101	130	924
15	50	42	150	6	37	80	90	160	3
16	90	99	150	33	38	70	74	125	31
17	80	98	130	2	39	100	110	160	24
18	60	65	120	1	40	120	116	160	23
19	60	76	150	3	41	90	105	160	8
20	80	79	130	36	42	100	90	150	49
21	130	131	180	4	43	80	83	130	18
22	80	86	150	3	44	120	118	–	–

3.4.2.2 Formalization of Relationship of Boundary Depths of Physical and Chemical Surfaces

The regression analysis of the resultant series of depths of physical and chemical surfaces showed the following (Bryantsev et al. 1988b):

- within the accuracy of 10 m, in summer the depth of maximal density gradient coincides with the position of the upper boundary of the permanent halocline;
- both surfaces (MP and PH) are located by 4 m deeper than the lower boundary of the cold intermediate layer,

$$\mathrm{Hg}\rho = \mathrm{Hgs} = \mathrm{H}_8 - 4, \tag{3.1}$$

  the correlation coefficient of Eq. 3.1 is 0.980 for 20% occurrence;
- under the suppressed oxygen exchange in the main pycnocline layer ($\mathrm{Ri} > 10$) the depth of the hydrogen sulfide upper boundary (H_s) is related to the depth of the lower boundary of the CIL (H_8) by equation:

$$\mathrm{H}_s = 0,88\mathrm{H}_8 + 59 \tag{3.2}$$

- under the facilitated oxygen exchange in the main pycnocline layer ($\mathrm{Ri} < 10$) the similar dependence is described by equation:

$$\mathrm{H}_s = 0,71\mathrm{H}_8 + 78 \tag{3.3}$$

The statistical characteristics of the relationships and samples are presented in Table 3.8. The correlation coefficients are high for all calculations, ranging from 0.974 at the suppressed vertical oxygen exchange to 0.76 at the favorable aeration conditions. For the whole sample it equals 0.833. Herewith, the mean standard deviations are 25 m. Thus, we obtained *the equations of relationship of topography of the hydrogen sulfide boundary with the position of characteristic physical surfaces* ($r = 0.76$–0.98) *under the different conditions of vertical oxygen exchange*.

Table 3.8 Statistical characteristics (H_{aver}, $\pm\sigma$) and correlation coefficients (r) between topography of the H_2S-zone boundary (H_s, m) and the upper boundary of the cold intermediate layer (H_8) under different conditions of oxygen exchange in June, 1985

Characteristic	Boundary	SAMPLE		
		Ri > 10 (21 stations)	All stations	Ri < 10 (18 stations)
H_{aver}	H_s	130	136	143
	H_8	81	86	92
$\pm\sigma$	H_s	18	23	28
	H_8	20	25	30
R	$Hs \leftrightarrow H_8$	0.974	0.833	0.760

3.4.2.3 Stability Testing of the Relationship Between the Positions of the Physical and Chemical Surfaces

For the stability testing of the revealed dependences during the different seasons at the second stage of the 44th cruise of R/V *Mikhail Lomonosov* (October, 1985) and in the special expeditions of AzCherNIRO (March–April, 1986) we have repeated the summer experiment, 1985 on 30 and 25 stations, respectively (Bryantsev et al. 1988b). The results of direct measurements of the position of the H_2S-zone boundary (H_s) during these seasons were compared with the results of calculations of its position by hydrological data, using the Eqs. 3.2–3.3.

The standard deviation of series of the direct H_s-measurements in autumn was 22 m, and in winter, 1986—30 m (Table 3.9). From 55 cases of comparison only in one case the deviation of the calculation result from the result of direct measurement fell outside the limits of these values (+33 m). herewith, the averaged measured and calculated depths of H_s both in the autumn and winter seasons coincided, being 128 and 129 m, respectively, for autumn; 131–134 m for winter (see Table 3.9). Thus, calculating the depth of the hydrogen sulfide boundaries by hydrological data (Eqs. 3.2 and 3.3), we commit the error, not exceeding an error under its direct determinations in the field conditions. The relationship revealed is stable in time and can be used for the retrospective calculation of the position of the upper H_2S-zone boundary in the Black Sea by hydrological data. Herewith, it is necessary to take into account that the more reliable results will be obtained under the spatial averaging of the calculated H_s-values.

3.4.3 The Retrospective Long-Term Dynamics of the Anaerobic Zone Boundary Calculated by Hydrological Data

Based on the revealed correlationship of the depth of the H_2S-zone boundary (H_s) with the position of the lower cold intermediate layer boundary (isotherm of 8°C- H_8) and used the available long-term hydrological data at the Yalta-Batumi cross-section (since 1954), we have calculated the retrospective dynamics of H_s for the summer season most provided with the hydrological data. The depth of the 8°C-isotherm was determined by means of interpolation on the vertical temperature profiles at the cross-section stations, and the H_s position was calculated by the regression Eq. 3.2. The section-averaged depth of the H_2S-zone boundary was determined with account of distance between stations by the method of numerical integration (Fig. 3.24) (Bryantsev et al. 1988a).

The interannual variability of the average position of H_s during 1954–1985 is characterized by the existence of three periods:

Table 3.9 The result of direct measurement (H_{mes}) and calculation by hydrological data (H_{calc}) of the H_2S- zone boundary (m) in the Black Sea

Item No	AUTUMN, 1985			Item No	WINTER, 1986		
	H_{mes}	H_{calc}	ΔH		H_{mes}	H_{calc}	ΔH
1	120	139	+19	1	200	189	−11
2	100	106	+6	2	170	174	+4
3	110	109	−1	3	–	166	–
4	90	100	+10	4	170	154	−16
5	110	105	−5	5	120	116	−4
6	110	99	−11	6	82	115	+33
7	110	102	−8	7	95	103	+8
8	130	135	+5	8	105	105	0
9	120	126	+6	9	140	138	−2
10	140	119	−21	10	106	122	+16
11	150	142	−8	11	107	114	+7
12	10	127	+17	12	107	116	+9
13	130	130	0	13	107	123	+16
14	150	135	−15	14	173	159	−14
15	130	121	−9	15	140	123	−17
16	125	125	0	16	117	123	+6
17	110	122	+12	17	135	131	−4
18	130	120	−10	18	106	123	+17
19	125	119	+6	19	138	137	−1
20	105	125	+20	20	140	136	−4
21	145	140	−5	21	120	129	+9
22	140	147	+7	22	110	114	+4
23	130	129	−1	23	150	137	−13
24	150	142	−8	24	180	176	−4
25	110	120	+10	25	133	128	−5
26	150	145	−5	Average	131	134	+3
27	135	138	+3	Σ	30	23	
28	175	167	_8				
28	190	184	−6				
30	130	125	−5				
Average	128	129	+1				
σ	22	19					

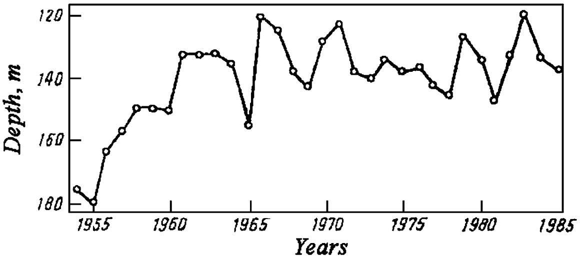
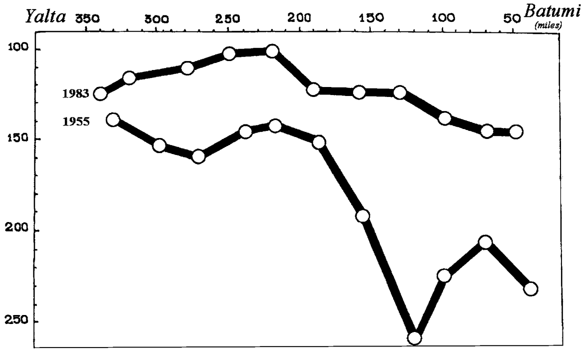


Fig. 3.24 Interannual dynamics of the upper anaerobic zone boundary in the eastern Black Sea reconstructed by hydrological data for the summer season (averaged over the Yalta-Batumi cross-section) (Bryantsev et al. 1988a)

Fig. 3.25 The H_2S—zone boundary at cross-section from Yalta to Batumi, reconstructed by hydrological data, in years with the deepest and shallowest position averaged over the eastern Black Sea in summer (Bryantsev et al. 1988a)



- from 1954 to 1961 there was a rapid rise of the H_2S-zone boundary, at rate of 4–5 m per year;
- during the following decade the rate of this tendency decreased to 1 m/year, and since the mid-1970s the rise almost broke;
- in periods of 1965–1971 and 1978–1984 the sharp variations of this surface were noted, and in 1971–1977 its position changed rather smooth;
- over the 30-year period of investigations the anaerobic zone boundary in the Black Sea has risen by about 40 m.

It is remarkable that exactly after 1965 (the beginning of the period of sharp changes in position of H_s) the hydrogen sulfide appearance at depth of 75 m began to fix for the first time in field conditions (Timoshchuk and Risik 1980; Zhorov and Boguslavsky 1985).

Taken advantage of the revealed relationship (Eq. 3.2), we calculated also the position of hydrogen sulfide boundary at each station of the cross-section from Yalta to Batumi in years with the deepest (1955) and shallowest (1983) position averaged over the eastern sea and constructed the corresponding graphs (Fig. 3.25).

The rise of the H_2S-zone boundary along the whole cross-section is obvious. Herewith, in its northern part, off the Crimean coast, the H_s- position for almost 30 years changed slightly (10–20 m), while in the southeastward direction, to Batumi, the position of this surface at different stations of the cross-section rose gradually. In 50 miles from Batumi, from 1955 to 1983 the H_s-boundary has risen by 90 m, and in 120 miles—by 140 m.

The performed calculations have allowed to assume that the cause of present hydrogen sulfide disbalance in the Black Sea and nature of complicated topography of its upper boundary was the following: *as a result of the general rise of the deep H_2S-containing water level, the C-layer, having occurred in dynamically more active zone, has extended due to the more intensive penetration of oxygen into it. It has led to an increase in rate of hydrogen sulfide oxidation there. Besides, the upper boundary of the C-layer under these conditions has become open to dynamic impact of synoptic eddy formations causing now its sharp local rise and deepening.*

3.5 Ecological Hysteria and Project on “Rescue” of the Black Sea from the Ecological Disaster

In the 1980s the American satellite *Landsat* has fixed the strange thing. The Dead Sea located in Jordan and related by its nature to the Black Sea, has changed the color in the space photos from blue to black during one turn of the satellite (Photo 3.6).

The subsequent study on the Earth showed that the basin “overturned”—deep salty waters saturated with hydrogen sulfide outcropped. The cause of accident consisted in disappearance of freshened surface layer as a result of 80% withdrawal of the river Jordan runoff for irrigation.

In the early 1990s the report on this accident, information about the anomalously shallow position of the upper boundary of the hydrogen sulfide zone noted in the Black Sea (Aizatulin and Fashchuk 1989), “pillars of fire” observed near Sevastopol and Yevpatoria and “bursts of flame of white color” with height up to 500 m and width of 1.5–2 km—sea fires, in the period of the Crimean earthquake, 1927 (Aizatulin and Fashchuk 1991) have been published in the scientific and popular scientific press of the USSR. As a result, the pages of many central mass were studded with the soul-chilling headlines predicting death of the Black Sea.

“What will be, if, God forbid, the Black Sea coast will have a new earthquake? Sea fires again? Or just one burst, one grandiose tongue? Hydrogen sulfide is flammable and poisonous… In the sky there will be hundreds of thousand tons of

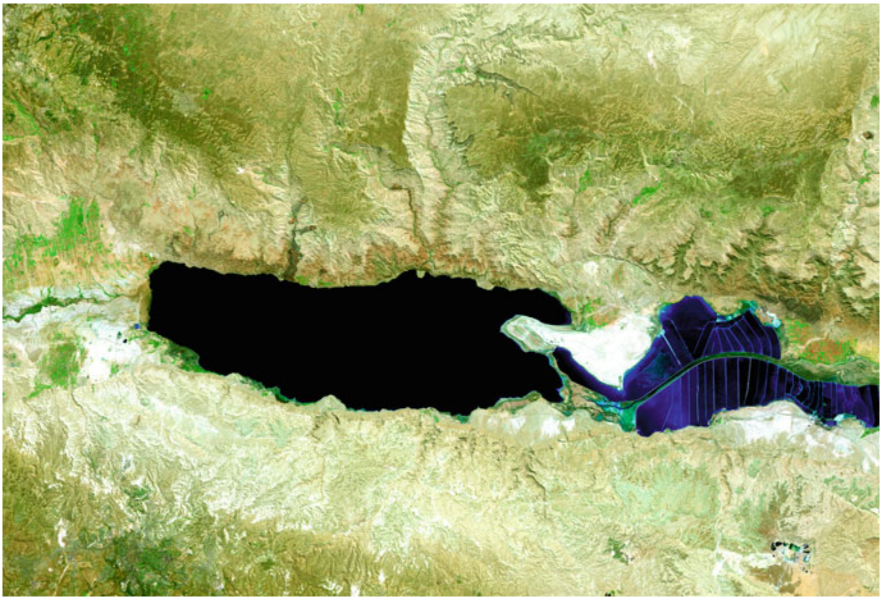


Photo 3.6 After the 80% withdrawal of the Jordan River runoff for irrigation the Dead Sea “overturned”—its salinity became uniform by vertical and hydrogen sulfide has reached the sea surface (visibleearth.nasa.gov)

sulfuric acid…!. “Small earthquake is enough in order that hydrogen sulfide will reach the surface of the Black Sea and inflame—its coast will turn into desert”. “The simple coincidence both in time and space… of sharp drop of atmospheric pressure and upward current…is enough… Having boiled, water will saturate the air with poisonous vapors of inflammable gas. Where the poisonous cloud will drift- Heaven only knows! It can cause victims at the coast or turn the passenger liner into the Flying Dutchman in a matter of seconds”.

The list of citations can be continued, adding it with extracts from dozens of letters in the Supreme Soviet of the USSR from worried inhabitants of the Black Sea coast. Probably, all these apocalyptic speculations would not deserve such attention, but, unfortunately, a number of rather serious events have become their consequence.

In 1990 the hydrogen sulfide threat to the Black Sea was represented as international (along with Chernobyl tragedy) in the closing address of the former president of the country to participants of the Global Forum on Environment and Development in order to survive. He said: “The upper boundary of hydrogen sulfide layer in the Black Sea for last decades has risen from depth of 200 m to 75 m from the surface. It is a little more, and through the Bosporus hydrogen sulfide will enter the Marmara, Aegean, and Mediterranean Seas”.

Moreover, the panic mood taken up by local newspapers of tens of maritime towns, in the late 1980s has aroused their population literally. During this period the author repeatedly witnessed “assaults” of groceries in Ochakov, Gelendzhik and other places of coast on the threshold of “approaching catastrophe”, and the group of scientists from the Sevastopol was worried seriously about the safety of the governmental summer residences and their owners on the South Coast of Crimea in case of hydrogen sulfide outcrop. Thus, the ecological illiteracy was transformed to a social problem—misinformation of the population, the government and the leader of the country, determined the ecological psychosis mongering.

In the circumstances concerned the unbounded sphere of activity for technocratic thought has opened. The way to “rescue” of the Black Sea was specified on pages of the same central newspapers. “Or we will become witnesses of the unprecedented ecological catastrophe…, or the great example of insightfulness and righteous technological power will be given to the world”. As “a great example”, the joint project of G.M. Krzhizhanovsky Power Engineering Institute and Ya.V. Samoilov Research Institute of Fertilizers and Insectofungicides “The Black Sea Oceanotechnology” was proposed. According to its idea, the anaerobic water rise should be stopped by pumping out the H_2S-saturated waters from depth of 1200, in the volume of 2,500 km^3 per year that corresponds to 12 annual runoffs of the Danube. In parallel, the knowingly unprofitable extraction of sulfur from this water of and production of hydrogen sulfide as energy carrier were planned. The authors guaranteed compensation for losses through the rescue of the Black Sea from an apocalypse.

For the first time the proposition regarding the power technological recycling of hydrogen sulfide from the Black Sea water has been stated by hydrophysicist A.S.

Vasilev at the 1st Congress of the Soviet Oceanologists in 1977. It was repeatedly discussed in the early 1980s but because of unprofitability of the large-scale production it stayed within the popular scientific publications and practical steps to its realization were not undertaken (Aizatulin and Leonov 1990). Thus, owing to the absolute ecological illiteracy not only the country population but the scientific elite advising the president, another "project of century" (totaling to 5 billion rubles at the prices 1990), undoubtedly more grandiose than the hard rejected project of northern river flow transfer to the south, was born. Its authors even counted on the economic effect in the amount of 89.9 million rubles and recoupment of the power chemical complex planned in Novorossisk, for 4–5 years. Fortunately, in the early 1990s the promoting of the project begun in 1984 г, has been ceased by efforts of many scientists. However, the authorities of Novorossisk (Photo 3.7), unlike, for example, administrations of the Ukrainian maritime cities, were ready as before to grant the city territory for construction of this giant power complex (thereupon, among scientists the project has been named "Novorossisk's Panama").Having organized in this city the International Socio-ecological Foundation "The Sea and Life" based on *NPO Energia*, in 1991–1992 the authors and supporters of the project gathered in Moscow and Sochi at the All-Union Conference "The state of the Black Sea Ecosystem and Possible Ways of Its Improvement" and the International Congress of the Black Sea rescue, where once again they tried to persuade the governmental structures of necessity to fund "the project of the century" and to attract foreign investors for this purpose. Not achieved the financing in 1992 г, the participants of the Congress of the Black Sea Rescue in its final resolution decided to create the International non-governmental organization "Committee on Protection of the Azov-Black Sea Basin". From the Congress Appeal to the Peoples, Parliaments, Governments of the Basin States the Tamara Globa's prophecy on "burn-up" of the Black Sea in 1993, stated at the first session of this forum, was removed. Nevertheless, it was easy to distinguish the true goal of creation of yet another Committee, obscured by traditional, high-minded slogans.

Today, fortunately, the project is not recalled any more but the credit in this goes to not so much the scientists as time. In new political and economic circumstances Russia is in no "projects of century" mood.

3.6 Geographic and Ecological Assessment of Ecological Catastrophe Probability in the Black Sea

The absurdity of suggestion on possible burning of the Black Sea and, especially, poisoning of the inhabitants of its coast with hydrogen sulfide became obvious after the analysis of many literary sources which are available at any institute of oceanographic profile of the Academy of Sciences, Hydrometeorological Service or Federal Agency for Fishery. But these data have not been of interest for the authors of the project completely, they merely replaced them with myths.

Photo 3.7 In 1989 Novorossisk was ready to grant the territory for construction of gigantic power complex on extraction and treatment of Black Sea hydrogen sulfide (photo from ISS—port of Novorossisk*)*

3.6.1 Seismic Activity of the Black Sea Coast and Cause of the "Sea Fires" During the Crimean Earthquake in 1927

We have analyzed the reality of apocalyptic forecasts and causes of the described catastrophic phenomena noted in the Black Sea, on the basis of the accumulated knowledge about hydrogen sulfide properties and basin nature (Aizatulin and Leonov 1990). As a result, it was possible to establish the following:

1. The seismicity of the Black Sea Coast area is limited to the periphery of the Black Sea depression, its central deepwater part is low-seismic (The Earth crust … 1975).
2. The Crimea, unlike other coastal areas of the sea, is characterized by narrowly localized seismic activity which zone there stretches along the steep continental slope as a continuous strip from Sevastopol to Feodosiya, with the maximum activity off Yalta.
3. For the last more than 100 years about 100 earthquakes in Crimea it has been fixed about 100 earthquakes with a magnitude of 5–8, and only in 1927 the outburst of seismic activity was accompanied by earthquake with a magnitude of 9, hundred of times exceeded the capacity of the known Tashkent earthquake.
4. As a result of tectonic movements on November 11th, 1927, the sea crustal block near the South Coast of Crimea in the earthquake epicenter (25 km off Yalta) and at distance to 100 km from the coast subsided, while the continental block upheaved (Fig. 3.26).

Thus, the effect of the natural disaster under consideration was local and did not extend on the main aquatory of the sea occupied with the hydrogen sulfide zone.

According to observational data, during the Crimean accident the bursts of white flame with height of 500 m and width of 1.5–2 km were noted upon the water at nighttime in westerly direction from Yevpatoria, Sevastopol and Cape Lukull (bearing of 255–260°).

When mapping this information (Fig. 3.27), it is easy to be convinced that "the sea has burnt" over the depths less than 100 m, where hydrogen sulfide in the near-bottom was never fixed. The nearest distance from the hydrogen sulfide zone boundary (isobaths of 150–200 m) to Sevastopol in this direction is 60–100, and to Yevpatoria—more than 200 km that excludes the possibility to see the flame even at night (Aizatulin and Fashchuk 1991).

The cause of "sea fires" becomes clear after the analysis of geological structure of the northwestern Black Sea shelf, typical gas-bearing area of the World Ocean. It showed that:

1. The northwestern Black Sea is meridionally crossed by 4 large geological faults (Fig. 3.27) separating the main structural elements of the Black Sea coastal area.
2. At present time, in zones of these faults the marine exploration and development of gas fields are conducted;

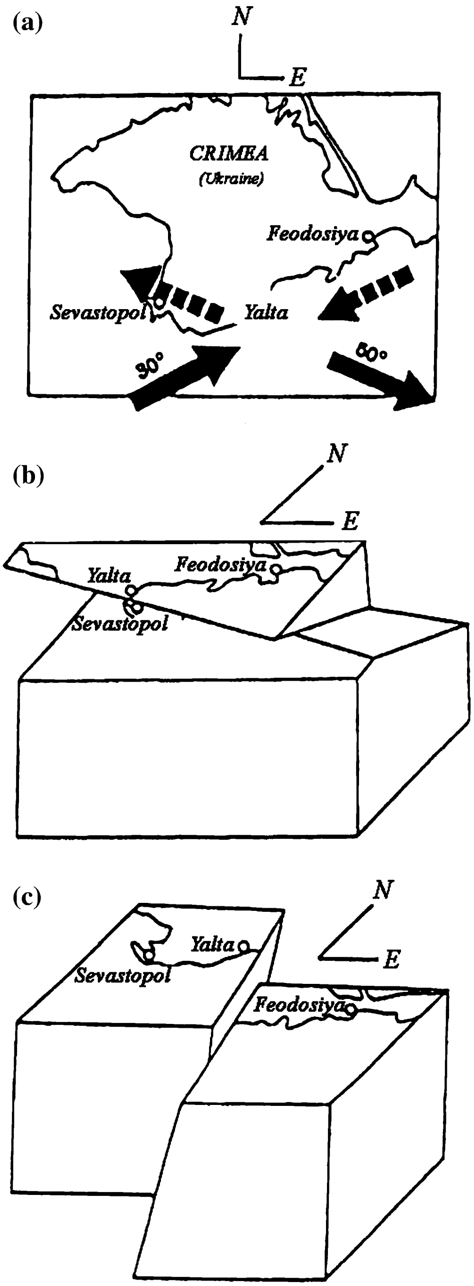


Fig. 3.26 Mechanism of the Crimean (Yalta) earthquake, 11 September, 1927 (The Earth crust … 1975) (**a** direction of greatest strain axes: continuous and dashed arrows—strains acting above and below picture plane, figures—angles of axis tilt to the horizon; **b**, **c** three-dimensional shifts along two possible planes of disruption)

3. The special expeditions carried out by Institute of Biology of the Southern Seas of the Ukrainian Academy of Sciences (Polikarpov et al. 1990) in the winter and summer seasons, 1989–1990 found about 150 underwater gas emissions, 80% of which consist of methane. With that:

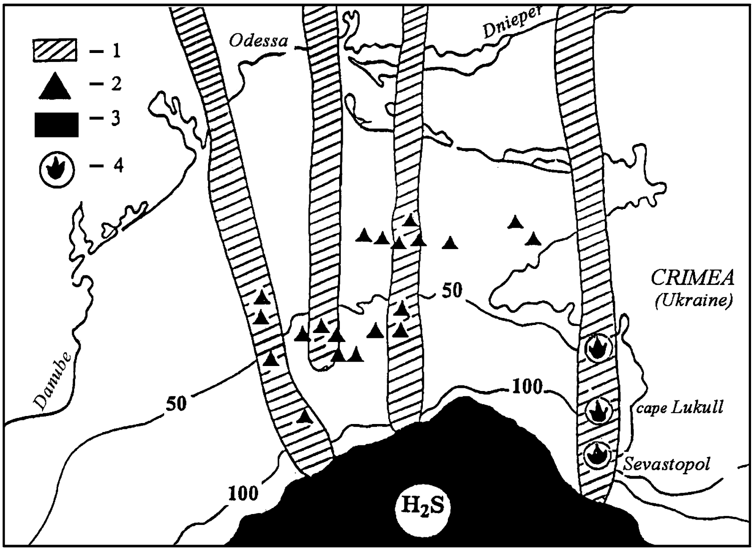


Fig. 3.27 Main tectonic faults (*1*), sites of marine exploration and extraction of natural gas (*2*), position of hydrogen sulfide zone (*3*) and sites of "sea fires" during Crimean earthquake, 1927 г (Aizatulin and Fashchuk 1991) (Figures—isobaths; *1* tectonic faults; *2* sites of marine exploration and extraction of natural gas; *3* hydrogen sulfide zone of the open Black Sea; *4* zones of "sea fires")

- in the northwestern Black Sea, on the site along the northwestern shelf the gas emissions were fixes at 32 points at depths of 100–300 м, with average cross-section area of gas flows of 50–70 m and sometimes 200–300 m;
- on another site in the same sea area at depths of 61–581 m 42 sources of gas emission were found, with the emission duration of 30–60 s and period of 1.5–2 h;
- in the Caucasian coast area, from Sukhumi to Batumi, at depths of 25–850 m 17 gas emissions were investigated. The strongest source was located at depth of 540 m and had a diameter of more than 400 m;
- in the area of the Karadag and Kerch Strait the similar event was fixed at 15 points at depths from 87 to 400 m, and along the coasts of Romania and Bulgaria—at 38 points located in the depth range of 99–590 m;

The "sea fires" during the earthquake period were observed on the aquatory located over the Krivorozhsk-Yevpatoria fault (see Fig. 3.27) bordering these sites The intensification of methane sources in the period of tectonic movements, up to outcrop of "tongues" and ignition, is quite real.

3.6.2 Toxicity and Explosiveness of Hydrogen Sulfide

The analysis based on the knowledge of its properties and study in the field conditions enabled to make the following conclusions (Aizatulin and Leonov 1990):

1. The maximum H_2S-concentration in the Black Sea water is 13 mg/L (see Sect. 3.4) that is 1000 times less that necessary for the 100%—saturation and release from water in the gaseous form.
2. The conditions for ignition or explosion of such solution are difficult for creating even in laboratory as the explosive concentration for hydrogen sulfide in the air is 4.5–45%, and ignition temperature—250°C.
3. For the real situation of the Black Sea, at the hypothetical instant outcrop of deep waters even the critical smelling H_2S- concentration of 2 mg/m^3 in the air over the sea is hard-reachable.
4. The human lethal hydrogen sulfide concentrations in the air are 670–900 mg/m^3, disturbances of the central nervous system are observed at 270 mg/m^3, and poisonings—at 70 mg/m^3.
5. The hydrogen sulfide content in medicinal waters (baths) of Matsesta resort (Photo 3.8) is : small dose—50–100, medium dose—150–200, and large dose—250–400 mg/L that is 5–40 times higher than in the Black Sea water but their use does nor result in explosions or poisonings.

Photo 3.8 In water from medicinal springs of resort of Matsesta (Sochi) the hydrogen sulfide concentrations are 100 times higher than in the Black Sea at depth of 2000 m ((sunywind-hosta.ru)—*top*; (foto.rambler.ru)—*bottom*)

6. The poisonings of people, change of burner flame color to green were noted at emergency emissions of hydrogen sulfide in collieries of England (“hydrosulphuric streams”); at incidental hydrogen sulfide emissions to the surface in upwelling zones along the Pacific coast of Latin America (“the Peruvian painter”) in the period of the El Nino event development there the darkening of coastal constructions and superstructures of passenger ships (due to oxidation of lead contained in paint) and fish kill were observed; the outcrops of H_2S-containing waters at distance of almost 300 km in the similar zones along the Atlantic coast of Africa (Namibia) were accompanied by the darkening of silver goods and spread of hydrogen sulfide smell over the land (to 40 km from the coast), but in all these cases there was no ignition or explosion of this gas.

Thus, toxicologically, hydrogen sulfide containing in deep waters of the Black sea does not pose a threat to the coastal population in any, even the most fantastic, situation.

3.6.3 Prime Causes of the Long-Term Dynamics of the H_2S-Boundary and Possibility of its Outcrop

The position of the main pycnocline in the Black Sea and, consequently, depth of the upper boundary of H_2S-containing waters may change under the influence of the long-term climatic variations resulting in an increase in the World Ocean level-strengthening of advection of Mediterranean waters into the Black Sea; change in character and intensity of atmospheric circulation over the sea—intensity of cyclonic circulation in the basin and, hence, rate of upwelling in its open part.

3.6.3.1 Global Climatic Variations

The correlation analysis of the long-term data on the average depth of the anaerobic zone at cross-section of Yalta-Batumi in August (H_s) retrospectively reconstructed by hydrological information with the long-term time series of the World Ocean level (ΔH) and data on mean monthly and mean annual pressure in Yalta for the during 1955–1985 period (P) showed (Fashchuk et al. 1990) the existence of statistically significant (95% significance level) relationships among them, formalized by expressions:

$$H_s = 0,37\Delta H + 121,4, \tag{3.4}$$

$$H_s = 5,87\,P_{\text{cpe}\partial.} - 5770, \tag{3.5}$$

$$H_s = 2,91\,P_v - 2790, \tag{3.6}$$

where $P_{\text{aver.}}$ and P_v—mean annual and mean May pressure (hPa) in Yalta, respectively.

The analysis of calculations made by Eqs. 6.4–6.6, shows:

1. The outcrop of deep waters in the open eastern Black Sea requires the World Ocean level rise of 330 mm. Under continuation of present tendency toward its rise (1.4–1.5 mm per year), it can occur in 220 years. However, taking into account the fact that periodicity of the process has much smaller period (Level fluctuations… 1982), the ecological disaster in the Black Sea under the influence of this climatic factor is unreal.
2. The response of H_2S-zone upper boundary to intensification of cyclonic atmospheric activity (pressure lowering) occurs with a lag of 2–3 months. The atmospheric impulse affecting the sea in May is realized (through the strengthening of cyclonic circulation and subsequent intensification of upward motions in the sea) as a change in the depth of H_2S-containing waters in August.
3. The outcrop of deep waters in the open eastern Black Sea under the atmospheric processes requires the lowering of mean monthly (in May) pressure in Yalta to 958.7 hPa. For the last 30 years this characteristic was not lower than 1002.8 hPa (1963).

Thus, the rise and outcrop of the anaerobic zone upper boundary in the Black Sea under the influence of the large-scale climatic processes determining its long-term dynamics seems unreal.

3.6.3.2 Change in Intensity of the Oxygen and Hydrogen Sulfide Sources

Another hypothetical mechanism of the C-layer upper boundary rise in the Black Sea may be associated with the increase in intensity of the hydrogen sulfide sources- intensification of life activity of sulfate-reducing bacteria owing to transportation of additional organic matter (catalyst of sulfate reduction) formed in the basin as a result of its eutrophication, into the deep layers of the sea. The test of this hypothesis in natural experiment is not possible now for the methodical reasons and due to a lack of the long-term time series of observations on this parameter. At the same time, today a number of mathematical models of the Black Sea hydrogen sulfide zone (Belyaev 1987; Leonov and Aizatulin 1987a, b; Leonov et al. 1988; Aizatulin and Leonov 1990) have been developed. By means of the last (most comprehensive) model we investigated (Aizatulin and Leonov 1990) the effects of change in intensity of the oxygen and hydrogen sulfide sources on position of the hydrogen sulfide boundary.

The materials obtained during our field investigations in the Black Sea served as a basis for the numerical model experiment carried out with the one-dimensional diffusive model of hydrosulphuric zone. The model considers the intensity of oxygen and hydrogen sulfide sources, rates of their consumption and oxidation, and physical and dynamical conditions of mass transport. In 11 simulation scenarios of model experiment *Turbulence* with the changeable vertical profile of the exchange coefficient (Fig. 3.28a) combined with 4 scenarios of experiment

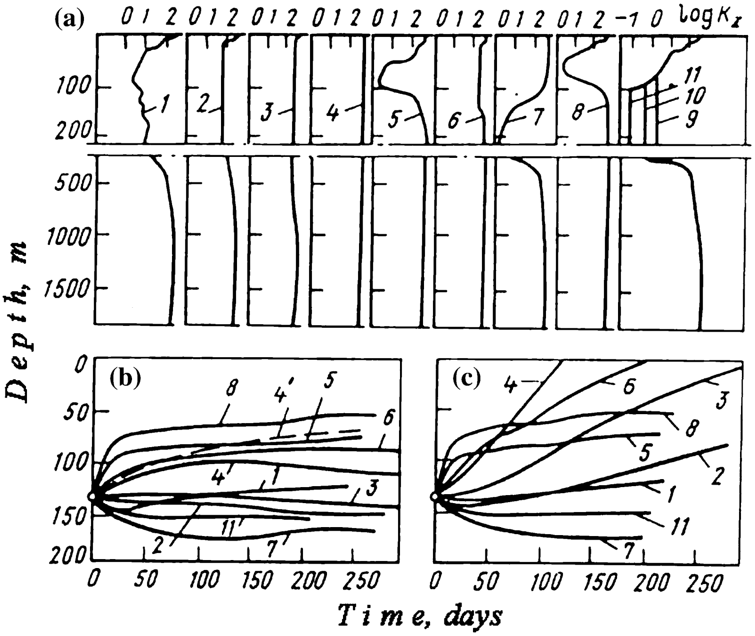


Fig. 3.28 Scenarios of distribution of the coefficient of vertical exchange (Kz, m^2/day) by depth (1–11) in the Black Sea (**a**) and results of scenario calculations of the H_2S-zone upper boundary dynamics at the real (2.74 mg/m^2 per hour) intensity of hydrogen sulfide sources (**b**) and in case of its thousand-fold increase (**c**) (Aizatulin and Leonov 1990) (Figures at curves—numbers of Kz scenarios; *1* present distribution of Kz)

Catastrophe (change in intensity of of hydrogen sulfide sources by 1–3 orders) we estimated the influence of change in the hydrological structure of the sea (up to a complete vertical homogeneity) on the dynamics of the hydrogen sulfide zone upper boundary at different intensities of the sources (Fig. 3.28b, c). *As a result, the role of the latter in this process was estimated that was yet impossible to investigate in the field conditions.*

The analysis of calculation results showed the following:

1. The position of the upper boundary of the C-layer is determined by the position of the vertical exchange intensity minimum and weakly depends on change in intensity of the hydrogen sulfide source.
2. Under the real hydrogen sulfide flux, corresponding to the current quantitative estimates, even in case of the completely mixed sea, the anaerobic zone boundary cannot outcrop, instead of this it sinks due to improvement of the deep layer ventilation (Fig. 3.28b).
3. Under the current conditions of vertical exchange (curve 1, Fig. 3.28a), even in case of a thousand-fold increase in intensity of hydrogen sulfide source, its upper boundary will not reach the sea surface (curve 1, Fig. 3.28c).

4. Under the conditions of the homogenous sea the outcrop of the anaerobic zone upper boundary is possible after 4 months of a thousand-fold increase in sulfate reduction intensity (curve 4, Fig. 3.28c).
5. In the sea conditions close to homogeneity, the outcrop of the anaerobic zone upper boundary is possible after 7–20 months of a thousand-fold increase in sulfate reduction intensity (curves 3, 6, Fig. 3.28c).

Thus, the ecological disaster in the Black Sea is possible only under fantastic conditions—almost full vertical alignment of density stratification and parallel 1000-fold strengthening of hydrogen sulfide flow.

3.7 Synoptic Variability of the H_2S-Boundary in the Black Sea

During the field investigations we ascertained that the most active dynamics of the hydrosulfuric zone was noted in coastal areas with a steep bottom slope—area of the South Coast of Crimea where offshore winds of the northern quarter were typical. These winds cause the upwelling phenomenon—lifting of deep waters to the surface. Herewith, the water temperature at the coastal beaches may decrease by 10°C within several hours (Photo 3.9).

3.7.1 Upwellings of the Black Sea

As it was mentioned earlier (Sect. 3.4.1), the upwelling phenomena, or offshore flow, were fixed episodically in the Black Sea in different years. So, in August, 1926 in the Feodosiya and Balaklava Bays the outcropped waters were lifted from depths of 20–25 m, and in 1932, 1938 the numerous Crimean upwellings were associated with waters lifted by offshore wind from depths of 50–75 m.

In June, 1949 the specialists of the Sevastopol Biological Station have fixed strong upwelling at the whole coast of the Black Sea from Odessa to Sochi. Herewith, within 6–12 h the water temperature at the Odessa beaches dropped from 20 to 6.7°C, at the South Coast of Crimea (SCC) off settlement Katsiveli—to 7.2–7.4°C, and in the Sochi area—to 10.7–11.3°C. The band of cold deep water risen to the surface from depths of 50–75 m after the long offshore flow (caused by winds parallel to the coast), have blocked the coastal zone with a width from 10 to 30 miles (18–55 km) and spread in the whole shallow northwestern Black Sea (Bogdanova 1959).

From the late 1980s summer upwellings off the beaches of the South Coast of Crimea began to be observed almost annually. The established fact of rise of hydrogen sulfide upper boundary (see Sect. 3.4.3) explains the cause of upwelling intensification reason off the South Coast of Crimea. The cold intermediate layer elevated synchronously with the H_2S-zone boundary by almost 40 m, became

Photo 3.9 During upwelling, despite the 30°C- heat, only a few people wish to have a swim at the beaches of the South Coast of Crimea, Yalta coast (www.crimeasea.ru)

more susceptible to the influence of offshore winds. In this case, even short strong night breeze can lift cold waters to the surface and kill the mood of vacationers in the morning.

On July 11th, 1986 we have fixed such phenomenon near Yalta (Fig. 3.29). During the nighttime after offshore (280°—10 m/s) wind the water temperature off the resort beaches has decreased from 22 to 10–11°C and remained at a such low level within 2 days.

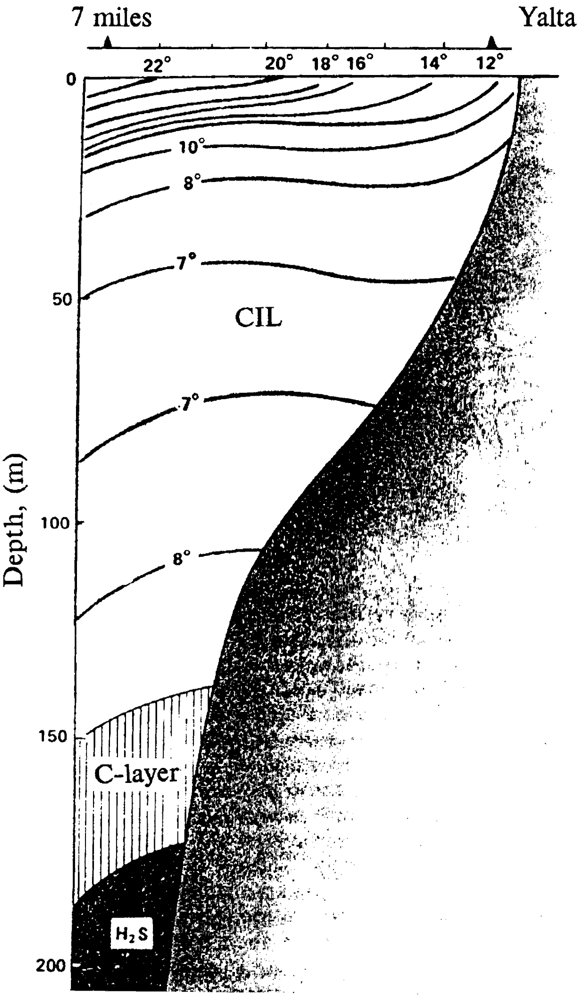
Number of days with offshore stormy winds in the northern (coast of the Crimea) and southeastern (coast of the North Caucasus) sea on the average for a year reaches 44–57, and in some years—62–71 days (Project "The Seas … 1991a, b). In summer these situations happen to 4, and in the winter—to 7 times per month. In the Kerch-Tuapse and Odessa areas of the sea the storms are noted 34–35, and in the SCC area –20–22 times per year (2 and 5 times per month in summer and winter, respectively).

3.7.2 Relationship of the H_2S-Boundary Topography with Summer Weather in the Coastal Black Sea

In the known anaerobic zone of the World ocean Walfish Bay at the Atlantic coast of South West Africa (coast of Namibia) under the influence of offshore winds hydrogen sulfide can rise to the sea surface over a distance of 300 km (Aizatulin and Skopintsev 1979). Naturally, there is a question, whether the similar situations are possible in the Black Sea and what hydrometeorological conditions are necessary for this.

To answer this question, in summer, 1986 at multi-day station near Yalta at a distance of 7 miles from the coast, on a beam of Cape Foros (Photo 3.10), in the zone of active upwelling development, we investigated the influence of weather conditions on topography of hydrogen sulfide boundary.

Fig. 3.29 Distribution of water temperature (isolines), position of the cold intermediate layer (CIL), the oxygen-hydrogen sulfide coexistence layer (C-layer) and anaerobic zone (H_2S) at cross-section seaward from Yalta after offshore wind, 11 July 1986 (Fashchuk 2002)



From the vessel stationary anchored at depth of 300 m during 20 days we carried out the C-layer sounding (spacing of 5 m, time interval of 12 h) with parallel hydrological observations to the bottom and registration of meteorological conditions by data of Yalta's hydrometeorological station.

For the whole operating time at multi-day station the upper boundary of the C-layer fluctuated from 145 to 165 m, locating on the average at depth of 158 m. The depth of the lower boundary of the layer ranged from 165 to 215 m, averaging 192 m, and the thickness of the C-layer varied from 12 to 60 m, with the average value of 33 m (Fig. 3.30).

Therewith, the oxygen and hydrogen sulfide stocks in the C-layer ranged accordingly from 1.2 to 9.1 and from 1.2 to 12.9 L/m^2, respectively, averaging 3.9 and 6.4 L/m^2. The maximum hydrogen sulfide oxidation rates of 12–16 g/m^2 per

Photo 3.10 In July, 1986 at distance of 7 miles from Cape Foros aboard the anchored vessel during 20 days we investigated the synoptic variability of the C-layer boundaries, in parallel with hydrometeorological conditions. *(cape Foros [crimeasea.ru])*

day were observed on its lower boundary at the time of its lowering (Fig. 3.30d), and the average integral rate of hydrogen sulfide oxidation was 375 g H_2S/m^2 per year, ranging from 70 to 964 g H_2S/m^2 per year.

The subsequent correlation analysis of the obtained hydrometeorological series and data on position of the C-layer upper boundary showed the following (Fashchuk et al. 1990):

1. There is a statistically significant (95% significance level) correlation between the position of the C-layer boundaries off the South Coast of Crimea and atmospheric pressure in Yalta ($P_{at.}$). The upper boundary of the hydrogen sulfide zone responds to its changes with a lag of 12 h and this response continues for 2 days.
2. In summer the position of this surface in the SCC area can be calculated 0.5–2 days in advance by meteorological data, using the regression equations:

$$H_s^{0,5} = 0,650\,P_{at.} - 465 \tag{3.7}$$

$$H_s^{1,0} = 0,743\,P_{at.} - 596 \tag{3.8}$$

$$H_s^{1,5} = 0,757\,P_{at.} - 610 \tag{3.9}$$

$$H_s^{2,0} = 0,730\,P_{at.} - 583 \tag{3.10}$$

where $P_{at.}$—pressure in Yalta (hPa); $H_s^{0.5-2.0}$—depth of the upper boundary of the hydrogen sulfide zone above the 300-m isobath after 0.5–2.0 days, respectively. The stability of the relationships over time will undoubtedly require experimental testing.

Simple calculations with Eqs. 3.7–3.10 show that for outcropping of the upper hydrogen sulfide boundary in the area under consideration the pressure in Yalta

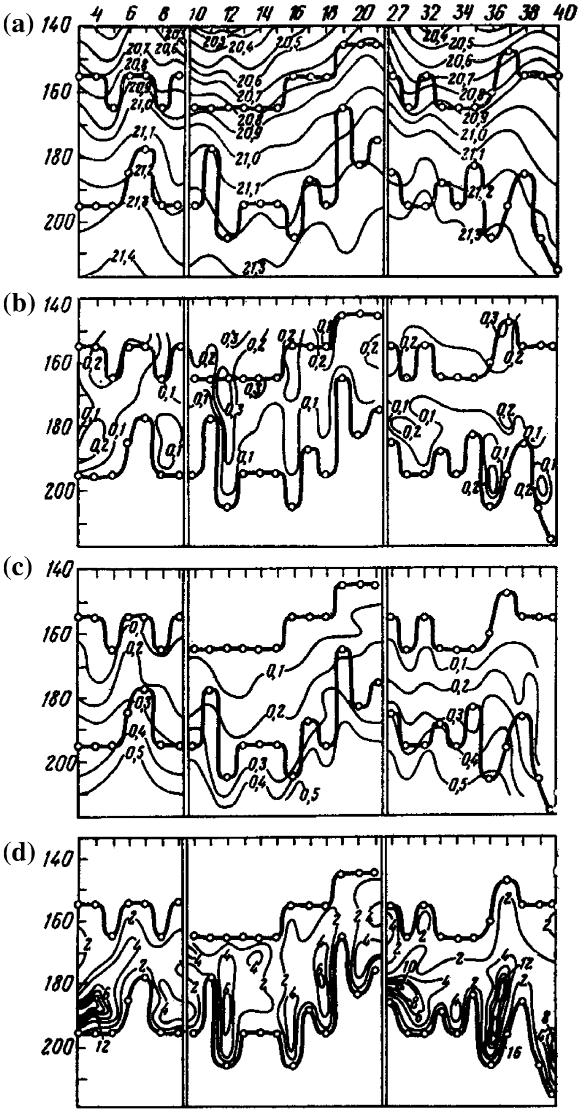


Fig. 3.30 Variations of the C-layer boundaries (*circles* and *thick line*) and its physical and chemical characteristics (isolines) at multi-day station off Yalta in July, 1986 (**a** salinity, ‰; **b** oxygen concentration, mL/L; **c** hydrogen sulfide concentration, mL/L; **d** rates of hydrogen sulfide oxidation, g H_2S/m^2 per day. *Horizontal scale* numbers of observation series; *Vertical scale* depth (m). (Fashchuk et al. 1990)

should fall to 800 hPa for, say, 2 days. The lowest pressure in Yalta over the last 100 years was 989.5 hPa (1969) (Project "The Seas… 1991a, b). Even in tropical cyclones of class 6 (the highest intensity) the pressure below 883 hPa was never fixed (Palmen and Newton 1973).

Thus, a local ecological disaster in the coastal dynamically active zone of the Black Sea under the influence of synoptic processes is also unreal.

3.7.3 Weather and Position of the H_2S-Boundary in the Open Black Sea

Once we were convinced that topography of the H_2S-zone boundary off the South Coast of Crimea was dependent on pressure in Yalta, it was assumed that this port was representative of the eastern Black Sea regarding the effect of synoptic processes on the position of hydrogen sulfide layer. The correlation analysis of the mean values of its depth (H_s) at cross-section from Yalta to Batumi in the summer period, as reconstructed from hydrological data (see Fig. 3.24), with the mean monthly and mean annual pressure values in Yalta for the 1955–1985 period indicated that H_s was related, at a significance level of 0.05 (95% confidence level), to the mean annual (P_{avg}) pressure and mean monthly pressure in May (P_v). The regression equations are

$$H_S = 5.87\,P_{avg} - 5770, \tag{3.11}$$

$$H_S = 2.91\,P_V - 2790, \tag{3.12}$$

Thus, our suggestion about the relation of the hydrogen sulfide boundary in the Black Sea with the intensity of atmospheric processes over its aquatory was confirmed. The atmospheric impetus received by the sea in May is embodied in its physical and dynamical water structure and in position of H_s in July–August, 1–2 months later (see Fig. 3.18)

Calculations with Eq. 3.12 indicate that outcropping of the hydrogen sulfide boundary in the open eastern part of the sea in summer requires the mean monthly pressure in May in Yalta to be 958.7 hPa. During the period of instrumental observations (Project "The Seas… 1991a, b) the lowest pressure has been 1002.8 hPa (1963). Thus, *an ecological disaster in the open sea as a result of synoptic processes is highly unlikely*.

3.8 Conclusions

The geographic and ecological analysis of the history of generation, evolution, and present state of anaerobic zone in the pen Black Sea, and not nearly complete accompanying list of the literature, evidences that the authors of the sensational apocalyptic articles and initiators of the multi-billion "project of the century" for the Black Sea rescue, advisers of the president for ecological questions (for certain, not ordinary scientists) at the end of the XX century have had at hand the materials dramatically demonstrating the absence of grounds for panic concerning the possible explosion or overturn of the reservoir (Photo 3.11). Nevertheless, all these knowledge accumulated for the 100-year history of its studying by several generations of researchers, during the most responsible time—the necessity of handling practical problems, have proved to be non-demanded. Instead, at the

Photo 3.11 Today the Black Sea suffers temporary troubles which will be "managed under its own power" (eltnews.com)

highest scientific levels the reliable quantitative knowledge of the concrete physiographic object have been replaced with the dangerous by their consequences for the nature myths in order to please a "technocratic power".

In the author's opinion, the reason of the occurred is that till the time of the problem initiation (1970–1989) all efforts of researchers of the World ocean, and the Black Sea in particular, have been concentrated on accumulation of factographic knowledge without serious attempts of its systemization, identification of mechanisms of interaction and regularities of functioning of various elements of marine ecosystem. The responsibility for such systemization lies first of all on geographic experts who at that time had no a reliable methodological apparatus for the system analysis of a huge volume of the collected data on the nature of the Black Sea hydrogen sulfide zone.

The results of realization of theoretical bases of marine ecological geography (see Chaps. 1–2) described in this Chapter have allowed to perform such systemization and to prove with reason the inadequacy of catastrophic scenarios of possible evolution of the anaerobic zone in the Black Sea. The result of the joint investigations carried out by efforts of specialists from 16 research institutes of different agencies in 1982–1989 was the conclusion that the cause of the observed shallow position of the hydrosulphuric zone was associated with the periodic long-term climatic variations. Today the boundary of "everlasting suffocation" is in its rising phase and the temporal troubles, according to academician V.I. Belyaev, will be managed by the Black Sea under its own power.

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Chapter 4
Seasonal Hydrogen Sulfide Zones of the Northwestern Black Sea Shelf: Nature, Dynamics, Prediction

In September, 1973 the expedition of the Odessa Branch of Institute of Biology of the Southern Seas (OdO INBYUM) has found for the first time mass kill of benthic organisms between mouths of the Kiliya arm of the Danube and Dniester estuary on the area of 3,500 km^2 with depths from 10 to 20 m (Salsky 1977). The number of dead hydrobionts during this period reached 500 thousand tons. Thus, in the Zhebriyansk bay adjoining the Danube, near the coast there was a large concentration of half dead passive bottom fish. Since then the similar events which were named "suffocation", during the summer—autumn period (from June to September) after offshore storms (under northerlies) are repeated from 4 to 10 times, being accompanied with "outbursts" of waters with unusual claybank color and hydrogen sulfide smell to the surface in the coastal zone (Fashchuk 1981). Near-bottom water, fishing gears, devices and ground lifted in the same time from the sea bottom on the open shelf sites at large distance from the coast have the similar smell (Photo 4.1).

According to estimations of OdO INBYUM specialists, till 1990 on every square kilometre of the area bottom 100–200 t of hydrobionts, including 10–15 t of fish, have been killed annually (Photo 4.2).

At the mean annual level it amounted 0.3–8 million t, and in all for the 1973–1990 period about 60 million t of bottom organisms, including about 5 million t of fish were lost on the northwestern shelf (NWS; Zaitsev 1992). In particular, from 1970 to 1980 the flounder stock in investigated area was reduced sixfold, from 7.7 to 1.2 thousand t. In catches of counting trawl this species was met only in the Cape Tarkhankut area and catch per unit effort decreased fourfold, compared to years before the suffocation development. Moreover, since the early 1960s the areas of commercial mussel fields and mollusk stocks were reduced by factor of 3.5 and 6, respectively, and the area of unique Zernov phyllophora field and seaweed stock in it—by factor of 2.5 and 20 (see Fig. 1.8, Chap. 1; Fashchuk et al. 1991). The facts of mass kill of bottom fishes, mollusks and seaweed in the coastal zone of the sea began to be noticed

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Photo 4.1 From the mid-1970s the northwestern shelf of the Black Sea has become and remains until now an arena of development of summer ecological crises—suffocation events caused by deterioration of oxygen regime in near-bottom layer up to formation of anaerobic zones there (Photo from ISS). *Left*—near-mouth area of the Dniester; *Top*: *left*—Odessa Bay; *right*—near-mouth area of the Dnieper, Tendra Spit, and Tendra Bay; *Right*: *top*—the Karkinit Bay; *bottom*—Tarkhankut peninsula

from the mid-1970s along coasts of Bulgaria and Romania also (Rozhdestvensky 1978; Atlas Oceanographic 1982). "Suffocations", mass kill of bottom fish species, mollusks and seaweed, at the coast of the northwestern shelf and in its open part appear incidentally, sporadically, redistributing suddenly along the coast from the Dnieper mouth to the Danube (Tolmazin et al. 1977; Rozhdestvensky 1978).

4.1 Research Strategy of Prime Causes of Ecological Crises

Based upon the specified external signs of suffocation manifestation, the majority of researchers of ecological crises believed that one of main causes of their development was associated with a decrease in dissolved oxygen concentration in near-bottom water (hypoxia) down to zero values (anoxia) and hydrogen sulfide formation during a spring-summer season. Nevertheless, the theory of the mechanism of oxygen regime deterioration in waters of the northwestern Black Sea shelf was

Photo 4.2 Suffocations have the most harmful effect on bottom fish species (flounder [www.upload.wikimedia.com], goby [www.sciencedaily.com]), sedentary representatives of a zoobenthos (shrimps [www.pokormiribok.com], crabs, mollusks) and attached forms of the higher seaweed

developed over more than 10 years. During this period many the most incredible panic suggestions “explaining” the prime causes of the phenomenon were brought out. They included such speculations as:

- existence of hydrogen sulfide sources in the investigated area, intensified by the geological reasons; oxygen was consumed for oxidation of hydrogen sulfide liberated from the bottom;
- penetration of deep oxygen-poor waters saturated with hydrogen sulfide from the open Black Sea onto the shelf, as a result of elevation of their upper boundary by climatic reasons;
- presence of bottom sites covered with silts on the shelf, which by some reason became the hydrogen sulfide producers in aquatic environment;
- presence of surface oil films preventing oxygen penetration from the air into the water, and many other things.

All these speculations, despite their contradiction to the facts of field observations, nevertheless, were actively discussed both in mass media and the scientific environment. But we have analyzed the more real explanations of the ecological crises causes based on the statements of theory of oxygen regime formation in sea waters.

4.1.1 Hypothesis of Complex Mechanism of Suffocation Development

The formation, development, and maintenance of water hypoxia in marine ecosystems require that rate of oxygen consumption would exceed the rate of its supply in the near-bottom layer. It can occur under the lessening of deep water ventilation in the process of vertical oxygen exchange (physic and dynamical mechanism), decrease in intensity of photosynthesis (physiochemical mechanism), or as a result of intensification of oxygen consumption at destruction of organic matter (biochemical mechanism).

4.1.1.1 Hypothesis of “Eutrophication”

The first researchers of mechanisms of hypoxia development on the Black Sea shelf believed that the prime cause of phenomenon is a summer intensification of destruction processes in the near-bottom layer of the shelf, accompanied by additional losses of oxygen in the process of oxidation of surplus organic matter. It enters the sea with river runoff and also accumulates on the bottom, dying off in the sea after phytoplankton blooms (“red tides”) caused by an increase in discharge of inorganic compounds into the sea, i.e. overfertilization (“eutrophication”) of coastal waters (Zaitsev 1976; Tolmazin 1977).

Following this hypothesis, the development mechanism of hypoxia is as follows: the increase in both organic and inorganic discharge of rivers and their anthropogenic chemical pollution → by this reason the following intensive summer development production processes in the shelf zone, especially in its near-mouth areas → as a result of rapid phytoplankton blooming ("red tides"), a large mount of surplus organic matter is formed in the area → after dying off phytoplankton is accumulated in the near-bottom layer → oxygen is consumed for its oxidation until the total depletion.

Despite the strength of the arguments (they are given in following section of the monograph), this hypothesis is not consistent. For example, such features of suffocations as unexpectedness of occurrence, their absence in some years with a high level of organic and inorganic pollution, occurrence in the areas remote from mouths of the large rivers, in bays without freshwater runoff and development of "red tides", remain unclear (Fashchuk 1982). At the same time, many authors investigated "red tides", as early as the 1960s noticed that formation of pycnocline layer due to intensive seasonal warming of surface water served as trigger for beginning of phytoplankton blooming (Dobrzhanskaya 1959). Moreover, eutrophication and phytoplankton blooming can be not the reason but a consequence of development of near-bottom hypoxia, as in these conditions there is a release of nutrients from bottom sediments into the water. In the Sea of Azov, for example, during 1969–1977, the period of the maximum development suffocation phenomena, at average 25–50% of nutrients carried by rivers were released from bottom sediments by this reason (Aleksandrova and Bronfman 1975). The similar facts were ascertained by scientists studied the causes of near-bottom hypoxia development at depth of 27 m in the Chesapeake Bay of the Atlantic Ocean (Taft et al. 1980; Photo 4.3).

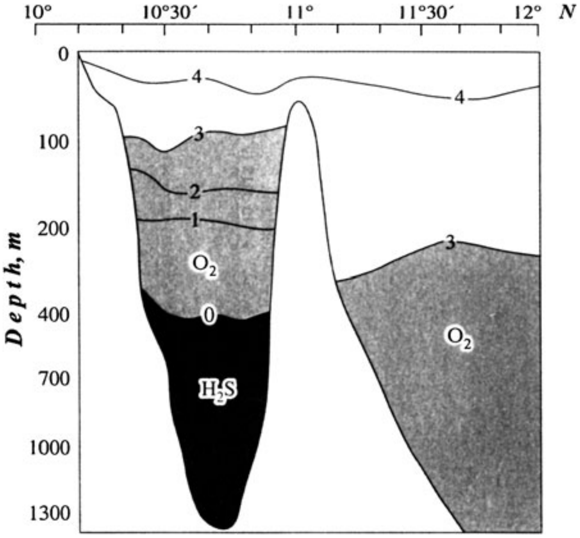
At last, by the time of the beginning of ecological crises on the northwestern shelf of the Black Sea, seasonal development of the hypoxia phenomenon has been fixed in crystal-clear water of Australian estuaries, located on the territory of national park and absolutely not subject to pollution and eutrophication (Reiner and Fitzhardinge 1981).

The oxygen minima were described in the intermediate layers of open waters of the Atlantic (400–800 m in a the Northern Hemisphere and 600–1,400 m in the Southern one), Indian (600–1,600 m), and Pacific(1,000–1,400 m in the Northern and 1,000–2,400 m in Southern Hemisphere) oceans (Ivanenkov et al. 1979), in the subsurface layer of the Arabian Sea (150–250 m), and also in the second largest after the Black Sea H_2S-containing basin of the World ocean—the Cariaco Basin in the Caribbean Sea (from 150 to 1,300 m; Aizatulin 1979), and in the Orca Basin in the Gulf of Mexico where eutrophication and pollution were absent.

In 1954, based on data on the presence of the high threshold separating the Cariaco Basin in the Caribbean Sea from the ocean, A. Redfild, only by one this physiographic fact preventing the ventilation of deep waters in the basin, "on a nib" (without the field investigations conducted later) has opened the second largest H_2S-containing reservoir of the World ocean (Fig. 4.1).

Photo 4.3 Chesapeake Bay at the Atlantic coast of the USA is one among many anaerobic areas of the World Ocean (by www.landsat.gsfc.nasa.gov)

Fig. 4.1 Oxygen distibution, mL/L in the Cariaco Basin (Aizatulin 1979)



4.1.1.2 Physico-dynamic Hypothesis

The analysis of hydrochemical regime features in the estuarine offshore zones of large rivers made as early as the late 1960s, showed that summer near-bottom hypoxia in these areas was a typical phenomenon (Simonov 1969). The current analysis of development of hypoxia zones in the World ocean confirms the conclusions of the Soviet researchers of semicentennial prescription (Diaz 2001; Gilbert 2001; Rabalais et al. 2002; Li et al. 2002; Chen et al. 2007; Photo 4.4). Thus all authors ascertained the presence of density stratification of waters (layer of density gradient) determining their stability and preventing mixing, as an obligatory condition for development of oxygen deficiency in the near-bottom layer. The same, adverse for vertical water mixing, physical conditions are formed also in coastal upwelling zones of the World Ocean.

The reason of the mentioned contradictions of the “eutrophication” hypothesis and the data of field observations was that its supporters, when estimating the oxygen balance in the near-bottom layer, assumed as variable only its consumption part—growth of oxygen consumption in the process of oxidation of surplus organic matter.

The attempts to investigate the influence of hydrological (physico-dynamic) factors on formation of oxygen regime in the near-bottom water layer were limited to several numerical calculations of drift currents velocities, discrete observations on currents, and individual field determinations of vertical stability (density distribution) in narrow shelf bands between deltas of the Dniester and Danube (Tolmazin 1977; Tolmazin et al. 1977). As a result, the supporters of the “eutrophication” hypothesis believed almost a priori that the vertical oxygen exchange in the investigated area is suppressed constantly and the reason of intensification of ecological crises in the 1970s consisted only in increase in the expenditure part of oxygen balance—its consumption. When measuring the current velocities in the zones of hypoxia, these researchers did not consider the fact that these velocities themselves were not an indicator of intensity of vertical water mixing (Photo 4.5).

The father of dynamical oceanology N. N. Zubov named turbulent mixing as “frictional” because it occurred only as a result of existence of current shear—a vertical gradient of this characteristic under the difference of motion speeds of the surface and near-bottom water layers (Zubov 1947). The Richardson number representing the ratio of vertical density gradient to the squared vertical gradient of current velocity can serve as an indicator of intensity of vertical oxygen exchange in the Black Sea (see Sect. 3.4.2). Its critical value for this basin equaled 10 (Bryantsev 1981).

4.1.1.3 Hypothesis of Complex Mechanism of Hypoxia Intensification

From the geographic and ecological model—“portrait” of the Black Sea (see Chap. 1) it is known that on its northwestern shelf such factors of hydrometeorological regime

Photo 4.4 The areas of near-bottom hypoxia zones on the Gulf of Mexico shelf from the Mississippi delta (*top*)—by www.earthasart.gsfc.nasa/gov, along the coast of the US States of Louisiana and Texas (*bottom*)—by www.geology.com, to the border with Mexico reach 18–21 thousand km^2

Photo 4.5 In confluences of the sweeping Caucasian rivers to the Black Sea, despite the sharp vertical density gradients (stability) of sea waters, hypoxia does not develop because of intensive mixing associated with vertical shear of current velocities (Photo from ISS)

as: – freshening influence and dynamic effect of several large rivers; – wind waves; – effect of water exchange with the open sea; – amount and regime of precipitation and evaporation, etc., are manifested in complex combinations. This results in the fact that stratification conditions—vertical density distribution and vertical shear of the currents determining the intensity of oxygen exchange between water layers (ventilation of deep waters), are formed there accidentally and irregularly and extend on its aquatory non-uniformly, changing with time. This can determine the noted features of suffocation events, indefinable from the positions of the "eutrophication" hypothesis.

In the late 1970s we have proposed a hypothesis, according to which the reason of the near-bottom hypoxia intensification and associated suffocations consisted first of all in a change of physiographic water structure of waters in the area, resulting in suppression of vertical oxygen exchange on the larger shelf aquatory in summer (Bryantsev and Fashchuk 1979). As a result of strengthening of water stratification and lessening of vertical current velocity gradient, a stable blocking layer, "hydrological cover" or "liquid ground", and the stagnation conditions preventing ventilation of the near-bottom layer are formed there during the summer period. The prime cause of such changes is associated with the anthropogenic regulation f river runoff during the summer season and climatic summer lessening of wind activity, characteristic for the area. Under these conditions the uncompensated oxygen consumption for mineralization of organic matter and respiration of marine organisms occurs, resulting in development of near-bottom hypoxia.

Herewith, the biogeochemical processes of bacterial sulfate reduction and escapement of anaerobic conditions (redox-cline) from the sediment layer into the water are intensified, accompanying by the formation and saturation of near-bottom water layer with hydrogen sulfide.

When developing the offered hypothesis, the role of inorganic and organic pollution (eutrophication) of shelf waters in change of their oxygen regime was not refused. Certainly, this process causes the growth of production and volumes of organic matter supply here, and after its dying off it results in the intensification of destruction processes in the near-bottom layer, accompanied by active oxygen consumption. There are no doubts that the development of near-bottom hypoxia depends directly on presence of oxidizing organic matter in the water. However, irrespective of its amount, *this phenomenon cannot be realized under the free oxygen access to the near-bottom layers of the sea*. The facts of appearance of oxygen deficit in estuarian waters of Australia, intermediate layers of the World Ocean and in its other non-eutrophicated areas indicate that the hypoxia phenomenon can take place at average or even relatively low concentrations of organic matter also. Its intensification thus can be related first of all to changes in physical and dynamical conditions of ventilation of the near-bottom seawater layer.

4.1.2 Experimental Study of Spatiotemporal Variability of Oxygen Regime in the Near-Bottom Water Layer

To study a role of various natural and anthropogenic factors in change in activity of the specified physical and dynamical and biochemical mechanisms of oxygen regime formation in the near-bottom water layer, it was necessary to solve following the problems:

- to estimate the interannual (summer) and seasonal (spring-autumn) variability of oxygen regime there;
- to reveal features of oceanographic water structure in zones with hypoxia and anaerobic conditions;
- to collect and analyze the long-term time series of observations on changes in the hydrometeorological and hydrobiological characteristics of marine environment reflecting the development intensity of the processes, priority for ventilation of deep seawaters (river runoff, atmospheric pressure, wind force and direction, sea level and temperature of its surface and near-bottom waters, content of inorganic and organic matter in the water, phytoplankton biomass);
- to make the correlation analysis between these characteristics and the parameters of oxygen regime in the near-bottom water layer of the northwestern shelf during the summer season and to identify the mechanism of their formation;
- to realize a mathematical model of shelf anaerobic zone dynamics and to make prognostic estimations of period and conditions of its existence.

With that end in view in 1974–1991 the specialists from South Research Institute of Fisheries and Oceanography (YugNIRO) under the supervision of the author (at that time the employee of this institute) and colleagues from the Odessa Branch of Institute of Biology of the Southern Seas (OdO INBYUM) carried out a complex of interagency investigations included: – biological and oceanographic monitoring of the northwestern Black Sea shelf; – statistical processing, analysis and visualization of its results; – systemization and analysis of departmental library materials of the Hydrometeorological Service system and data banks of the long-term observations on marine environmental conditions and state of biological components of the northwestern Black Sea shelf ecosystem, conducted by OdO INBYUM and YugNIRO; – development of numerical calculations scenarios for mathematical modeling of chemical dynamics of shallow anaerobic zone under different hydrometeorological conditions, based on the collected geographic and ecological information. During 1974–1991 YugNIRO alone conducted about 60 special expeditions in which the role of physiodynamic and biochemical mechanisms in development of ecological crises was investigated (Fig. 4.2; Photos 4.6, 4.7).

The works on the open shelf were conducted under the scheme of stations shown in Fig. 4.2a, with distance between stations of 3–5 miles, and their results (oxygen regime) were used as background at carrying out of investigations in the coastal areas. The latter were carried out after the beginning of hypoxia development there (July) and continued till its full termination (November). The stations of microsurveys were spaced 1–2 miles apart (Fig. 4.2b; Photo 4.8), time of one survey did not exceed 1 day, and the interval between them was 5–10 days.

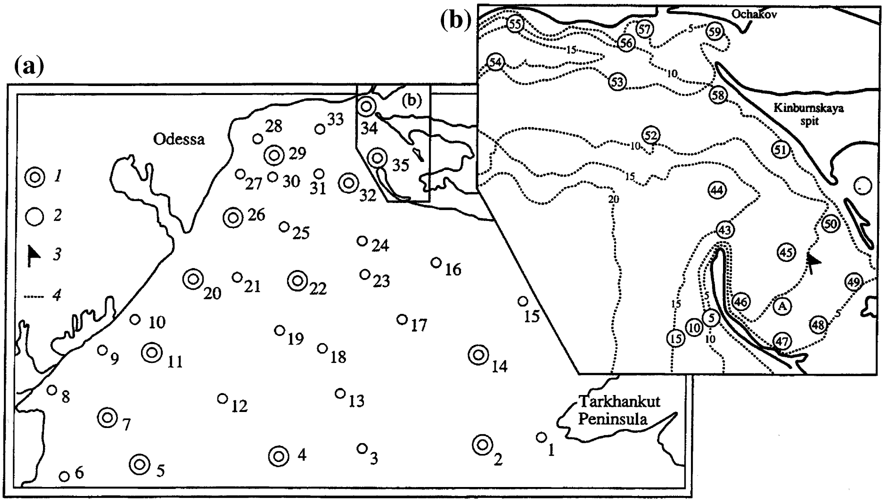


Fig. 4.2 Scheme of stations of oceanographic monitoring of the northwestern Black Sea shelf in 1979–1989 (**a**) and targeted field experiment of 1990 in the near-mouth zone of the Dnieper—Tendra Bay (**b**). *1*—Stations with determination of biochemical parameters; *2*—oceanographic stations; *3*—multiday oceanographic station, 1980; *4*—isobaths. *Figures*—station numbers

Photo 4.6 Small seiner refitted for scientific research is the best floating craft for the sea shelf study (Photo by author)

Photo 4.7 Submersible *Reef* with the maximum submergence depth of 70 m has participated in the investigations of causes of ecological crises on the northwestern shelf of the Black Sea also (Photo by author)

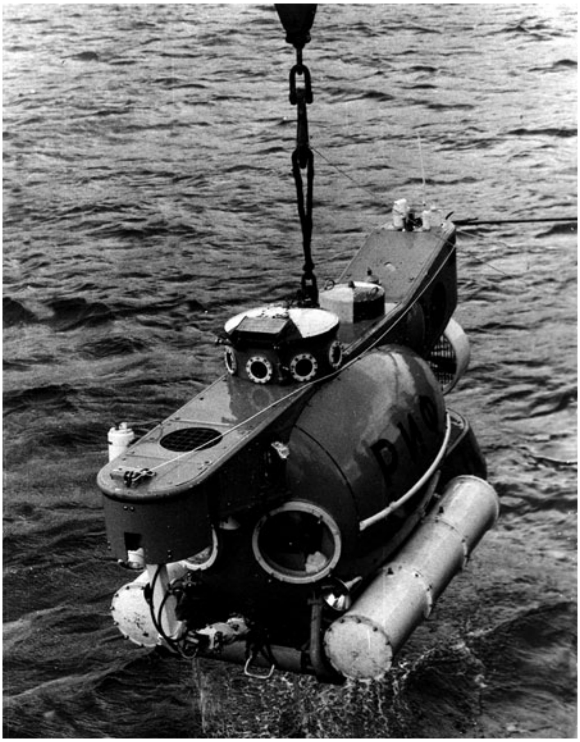


Photo 4.8 At the end of the XX century the near-mouth zone of the Dnieper and the Tendra Bay, the traditional areas of mussel cultivation, became the "dead zones" by reason of development of hypoxia and anaerobic zones there in summer. Photo from ISS (*Bottom*—Open northwestern shelf of the Black Sea; *Left upper corner*—the Southern Bug River; *Top*: mouth of the Dnieper and the Dnieper—Bug Liman, Kinburn Spit, Yagorlytsky Bay, Dolgyi Island, Tendra Bay, Tendra Spit)

In parallel with this, the data about weather in standard observational time of observations at hydrometeostation Ochakov were fixed, and the occurrence of winds of 16 bearings in characteristic months (June–September) was calculated for the whole period of development of ecological crises (from 1970).

The correlation analysis of characteristics of the meteorological, hydrological and hydrochemical regimes obtained during the experiment, allowed to *investigate the character of synoptic variability of anaerobic zone position, prospects of their*

Photo 4.9 Mechanism of Alekseev self-recording current meter BPV-2r (letter-printing current meter) combines cock, anemometer, compass, printing machine, and alarm clock in a single device cast into the sea in the sealed container, by the means of magnets, driving gears, small triggers, screws, bolts, ink, paper strip

evolution under the influence of hydrometeorological factors, to develop recommendations on the rational siting of mussel plantations (Fashchuk 1982, 1995).

The research process consisted of several stages:

1. During the spring-summer season (period of the beginning and maximum development of the phenomena), 1978–1981 we carried out 12 oceanographic surveys in the specified area, in which, according to the special scheme of stations (see Fig. 4.2a) with spacing of 3–5 miles, the importance of vertical oxygen exchange under formation of hypoxia and anaerobic zones there was assessed. For the quantitative characteristic of this process the Richardson number (Ri) was used (see Chap. 3).

In field conditions the current velocities were measured with the self-recording current meter above and below pycnocline at depths with spacing of 1–2 m, printing interval of 5 min, and the following averaging of 3–5 prints (Photo 4.9). The intensity of oxygen exchange was estimated after comparison of the calculated Ri values with its critical value.

By materials of more than 800 oceanographic stations included more than 500 parallel measurements of direction and velocities of currents with data on temperature, salinity and dissolved oxygen (more than 6,000 measurements, in all), *as a result of experiment the spatial relationship of physico-dynamic state of seawaters with the oxygen regime in the near-bottom layer has been investigated.*

2. From 25 July to 14 September, 1980 at stationary station (depth of 10 meters), in the hypoxia development zone (the Tendra Bay), from board of the anchored vessel, we fixed daily, with vertical spacing of 1 m, the characteristics contributing to the Richardson number, in parallel with measurement of dissolved oxygen concentration. As a result of experiment, *the temporal relationship of physico-dynamic state of seawaters with the oxygen regime in the near-bottom layer has been investigated.*

3. In 1981, at 13 shelf stations in the northwestern Black Sea in May, prior to the beginning of hypoxia development, and in July, at the time of its most intensive development, at depths above and below pycnocline the mentioned physiodynamic parameters were determined simultaneously with biochemical characteristics—values of BOD_5 and concentration of organic matter (by permanganate value). The comparison of results of the Ri number calculations and indicators of destruction processes intensity by data of about 200 such parallel determinations allowed to estimate *the contribution of biochemical mechanisms to development of ecological crises* (Fashchuk and Sebakh 1984).

4. The conditions of hydrogen sulfide zone formation on the shelf and its hydrochemical features were studied on 8–9 September, 1983 at daily station in the near-mouth zone of the Dniester. At that time, the aquatory with such conditions occupied 70% of the shelf area, the upper boundary of hydrogen sulfide was located at depths of 4 and 15 m, with the sea depths of 12 and 27 m, respectively (Selin et al. 1988). The near-bottom hydrogen sulfide concentration on the station (depth of 12 m) was 1.77 mL/L.

The observations were conducted with discreteness of 6 h. The water sampling was carried out with vertical spacing of 1–2 m by 10-L Van Dorne Teflon bottles, with determination of concentrations of O_2, H_2S, NH_4, NO_2, NO_3, N_{tot}, N_{inorg}, P_{tot}. Water temperature and salinity were fixed also. Oxygen in the presence of hydrogen sulfide was determined by iodometric method with addition of $HgCl_2$. When determining nutrient concentrations in the presence hydrogen sulfide, the samples were bubbled. The results of experiment were used for modeling of chemical dynamics of the hydrogen sulfide zone on the shoal that allowed to estimate the possible time of existence of anaerobic zones, depending on hydrometeorological factors and hydrogen sulfide concentration, and to calculate the rates of hydrogen sulfide production and oxidation which have not yet been determined experimentally there (Selin et al. 1988; Leonov and Aizatulin 1995).

5. To test the adequacy of model calculations and experimental estimation of synoptic dynamics of anaerobic zone of the shoal, in summer and autumn, 1990–1991, on the northwestern Black Sea shelf the targeted field experiment included 3 oceanographic surveys of the open shelf (May, June, and July) and 11 repeated microsurveys of the Tendra Bay and the near-mouth area of Dnieper, zones of aquaculture farms on artificial cultivation of mussels, has been carried out.

4.2 Peculiarities of Oxygen Regime in Near-Bottom Shelf Waters

The retrospective analysis of oxygen regime features in waters of the northwestern shelf (NWS) allowed to conclude that the confluence area of such rivers as the Dnieper, Dniester and Danube is not an exception in this context (Fashchuk 1985). For the first time the development of summer hypoxia in their near-mouth zones was mentioned as early as 1926 when in the area of Odessa and the Dniester liman a decrease in the summer near-bottom oxygen concentration to 3.4 mL/L was fixed (Knipovich 1930, 1932). In May and August, 1957 (Shulgina 1961) the hypoxia development (1.84–2.47 mL/L) was also noted there, and in the summer-autumn period of 1957–1962 in the Dniester Liman mouth, off the Snake Island and the Tendra Spit the near-bottom oxygen content decreased to 2.42, 2.12 and 2.88 mL/L, respectively (Novitsky 1968). In August 1970 and 1974 the bottom O_2-concentrations on the Odessa bank and Dnieper offing did not exceed 1 mL/L (Izmestyeva 1983).

Thus, from the beginning of regular investigations (1920s–1930s) to the mid-1960s the near-bottom hypoxia was noticed periodically on local sites of this area during the spring-summer period, without causing the serious ecological consequences. However, since the mid-1970s development the spatial and temporal l scales of hypoxia development and its intensity have increased essentially, up to development of anaerobic zones, and its consequences have got the character of ecological crises.

After statistical processing of the time series of long-term observations on the oxygen content in waters of the northwestern Black Sea shelf, conducted by YugNIRO (from 1955), the statistically significant trends of this characteristic were revealed:

1. From the second half of the 1960 the sharp decrease in the near bottom oxygen concentrations is observed during summer north of the line of Tarhankut–Danube River (Fig. 4.3).
2. The progressive negative tendency of this characteristic in the Dniester–Danube interfluve and in the area of Odessa—the Dnieper offing reaches 3.65 and 4.75 mL/L for 23 years, respectively Eastward (Karkinit Bay), the rate of oxygen concentration decrease (trend) reduces, and in the Cape Tarkhankut area the trend falls to zero (Fig. 4.3, right).

The results of monitoring conducted in 1978–1991 and analysis of literature data have allowed to reveal the essential changes in the character of hypoxia zone development in the investigated area and relationships of this process with volumes of the river runoff:

1. From 1978, the hypoxia in the northwestern Black Sea has developed annually (Fig. 4.4).
2. Originating in May at traditional near-mouth sites of the shelf and occupying at this time 6–20% of its aquatory area, it is propagated by the late summer to its open part (depths of 30–40 m), into the bays without freshwater inflow, covering up to 60–80% of the aquatory area (see Fig. 1.6, Chap. 1).
3. At the sea depth of 10–15 m the thickness of hypoxia layer can reach 5–6 m, and at depths of 30–40 m the oxygen deficit in the near-bottom layer has vertical development up to 12–15 m (Fig. 4.5).
4. In the late summer the formation of hydrogen sulfide begins in the shelf areas with hypoxia. In 1983, for instance, the area of anaerobic zone there was 5,000 km^2 (10% of the aquatory area to isobath of 50 m), the reserves of

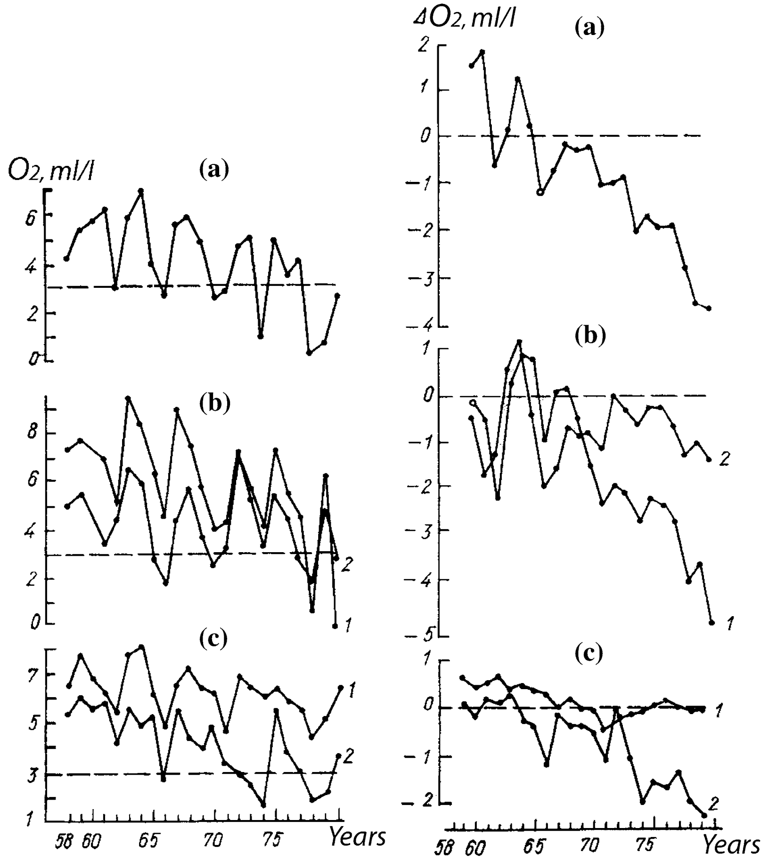


Fig. 4.3 Dynamics of oxygen concentrations (*left*) and their trends (*right*) in the near-*bottom* layer of the northwestern Black Sea shelf during the summer period, 1958–1980 (Fashchuk 1985) (*Sections*: **a** Tendra Spit—Odessa; **b** Karkinit Bay—Shagany Lake; **c** Cape Tarkhankut—Sulina. At *section***a**—diagram of oxygen concentrations averaged over three stations (Nos. 29, 31, 32 in Fig. 4.2a). At *sections* **b** and **c**: *1* and *2*—diagrams of oxygen concentrations at easternmost (No. 15 and No. 1 in Fig. 4.2a) and westernmost (No. 11 and No. 5 in Fig. 4.2a) stations of cross-sections, respectively

hydrogen sulfide exceeded 15,000 t, and thickness of the H_2S-containing water layer ranged from 2 to 10 m with the sea depths of 8 and 25 m, respectively.

5. The hydrogen sulfide concentrations in the near-bottom layer varied from 0.2 in the initial period of phenomenon development (July) to 2.0 mL/L in the late summer—early autumn (see Fig. 4.5). Such values are observed in the central deepwater areas of the Black Sea at depth of 200 m. In August 1990, in the open part of the shelf, they were 0.2–0.7 mL/L, in this case, 40% of its area (40,000 km^2) were occupied by waters containing hydrogen sulfide (see Fig. 1.6, Chap. 1; Fig. 4.6) times larger, compared with the area of hypoxia zones developing on the Yangtze offing in the East China Sea (Li et al. 2002).

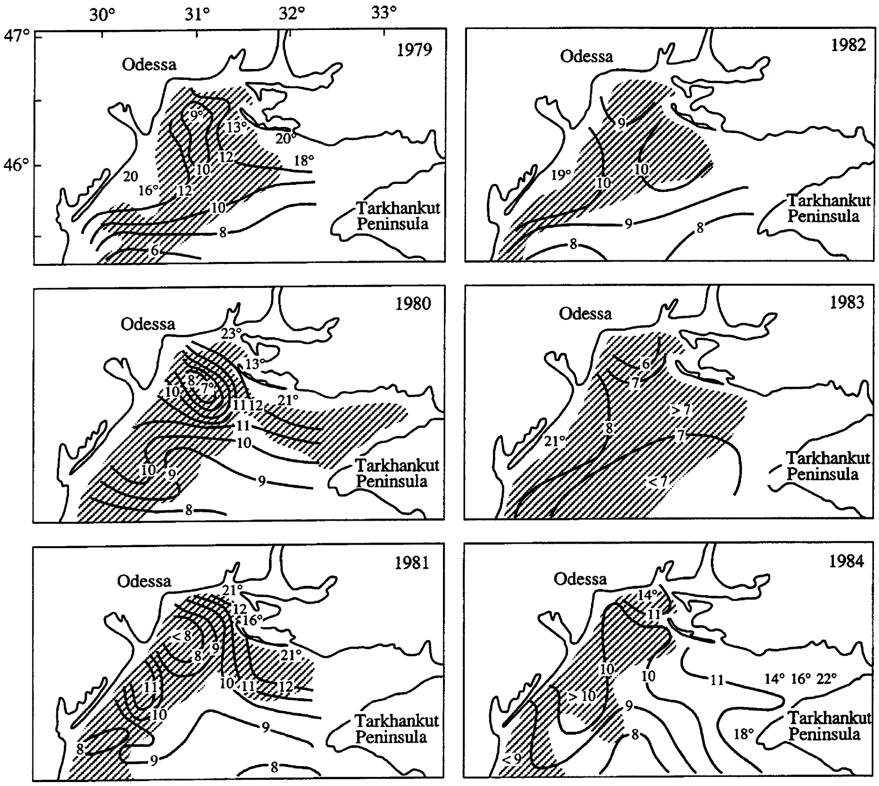


Fig. 4.4 Distribution of hypoxia zones (the O_2 concentration less than 2 mL/L are shaded) and near—bottom water temperature (isolines, °C) in the northwestern Black Sea in different years (Fashchuk 1995)

6. The areas with hypoxia and anaerobic conditions on the northwestern shelf are local and not related to “permanent” suffocation, anaerobic zone of the open Black Sea, which is located deeper than 150–180 m and to 2,000 m.
7. The scales of interannual variations in sizes of water areas with hypoxia are changed in the late summer, depending on the runoff volumes of main rivers in the characteristic months (June-July for the Danube, and May–June for the Dniester) (Berlinsky 1989; Berlinsky and Dykhanov 1991):

   - in the Danube area the near-bottom hypoxia continues until September under the Danube runoff in June–July of 70 km^3;
   - for the central areas of the northwestern shelf the similar conditions are provided under the Dniester runoff in May–June of 4 km^3.

8. The near-bottom oxygen concentration in the Odessa area in August depends directly on the total intake of organic matter with waters of the Dnieper in July–August (Kovalchuk 1985, 1986).

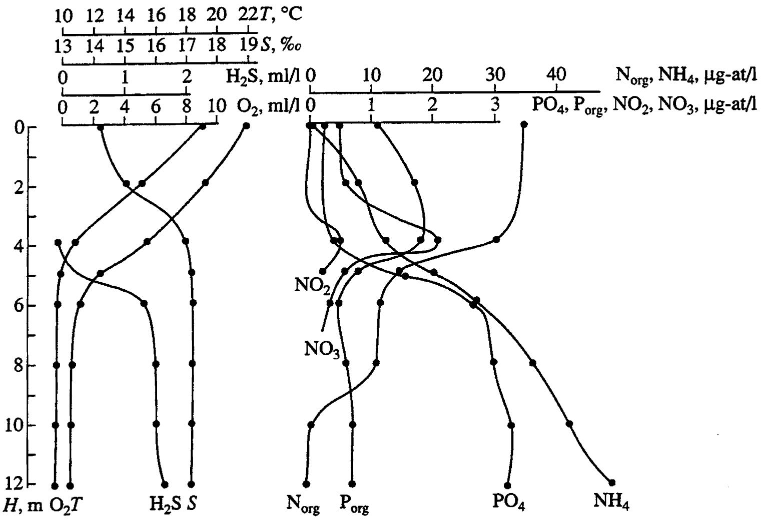


Fig. 4.5 Vertical distribution of oceanographic characteristics in the anaerobic zone on the Dniester offing in September 1983 (Fashchuk 1995)

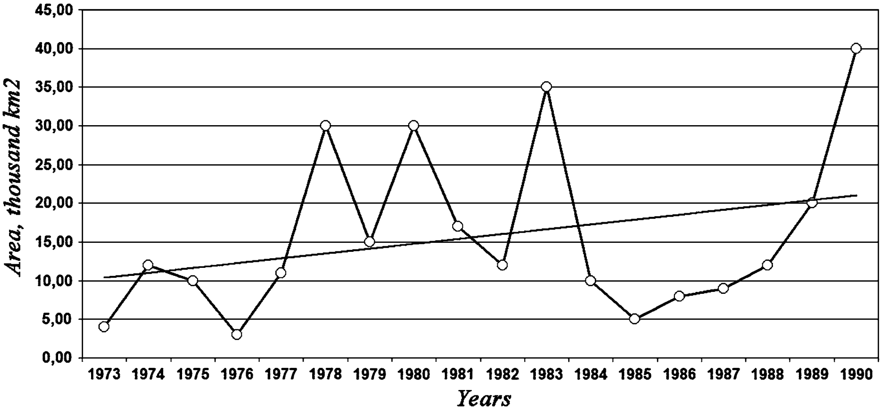


Fig. 4.6 Dynamics of the areas of near-bottom hypoxia on the northwestern shelf of the Black Sea (Zaitsev 1992)

4.3 Tendencies in Oceanographic Characteristics and Water Structure

As a result of independent statistical processing of databanks on the hydrology of the Black Sea carried out by various authors in the late XX century, almost identical conclusions about the long-term tendencies in changes of physiodynamic conditions of the northwestern shelf were obtained (Photo 4.10).

Photo 4.10 Today the Tendra lighthouse crests the western tip of the spit (length of 65 km, width of 1.8 km) on which ancient Greeks organized athletic meet in honor of their mythological hero Achilles (*top*—www.dikarem.net, *bottom*—photo from ISS)

4.3.1 Physico-dynamic Parameters

1. From the second half of the 1960s the stable freshening of surface (above seasonal thermocline) water layer has been observed in summer in the region under investigation. The negative salinity trend reaches 0.3‰ per year (Kovalchuk 1985; Altman et al. 1988).
2. In parallel with this, the salinity increase in the near-bottom layer was noted (Bryantsev et al. 1984; Altman et al. 1988; Selin et al. 1992). For the last 23 years in the Danube offing zone it increased by 1.06‰. At intermediate depths of 10–20 m in the open areas of the northwestern Black Sea the positive salinity trend for 20 years reached 0.79‰. Beginning from 1967, the salinity increase in the near-bottom layer has been stabilized, while at intermediate depths it continues to rise—the thickness of saline near-bottom water layer increases.
3. For the last 25 years the volume of water with salinity of 18.3–18.9‰ has increased in the summer period by 10% in the shallow shelf areas, while the volume of overlying water with lower salinity (17.3–18.2‰) has reduced proportionally (Fashchuk et al. 1986). There is an increase in thickness of the deep saline water layer due to advection of water the open sea onto the shelf (depths less than 50 m).
4. The positive trend of vertical salinity gradient for the indicated period was revealed in the 0–30 m layer (Altman et al. 1988). The salinity difference between surface and near-bottom layers prior to 1982, according to averaged and actual data, increased by 1–1.8 и 3‰, respectively (Selin et al. 1992).
5. Negative tendency in the near-bottom water temperature changes was noted in the open areas of the northwestern Black Sea. For the 1960–1980 period it made up 0.1°C per year (Altman et al. 1988).
6. Aeration of deep water layer as a result of vertical oxygen exchange during the summer period was suppressed (Fashchuk 1981). The Richardson number value characterizing intensity of this process, exceeded the critical value of 10 on the larger shelf aquatory. With that, in different months from 72 to 100% of near-bottom hypoxia zones coincided with zones of the suppressed oxygen exchange (Fig. 4.7).
7. In spring, the density stratification contributed to suppression of vertical oxygen exchange most significantly. In that time the hypoxia zones coincided with areas of high water stability (Fig. 4.8a). In summer, the vertical exchange was suppressed as a result of water stagnation. With that, the hypoxia zones coincided with areas of the weakened shear of currents (Fig. 4.8b).
8. Compared with the 1960s–1970s (Atsikhovskaya and Tolmazin 1970), the velocities of discharge currents in the near-mouth areas of the Dnieper decreased more than 2 times in summer and did not exceed 10 cm/s at calm weather, and 40 cm/s during storms (Fashchuk 1995).
9. The vertical gradients of density, temperature, and salinity here could reach 6 conventional units, 15°C, and 6‰ per 1 m, respectively (Fashchuk et al. 1986).

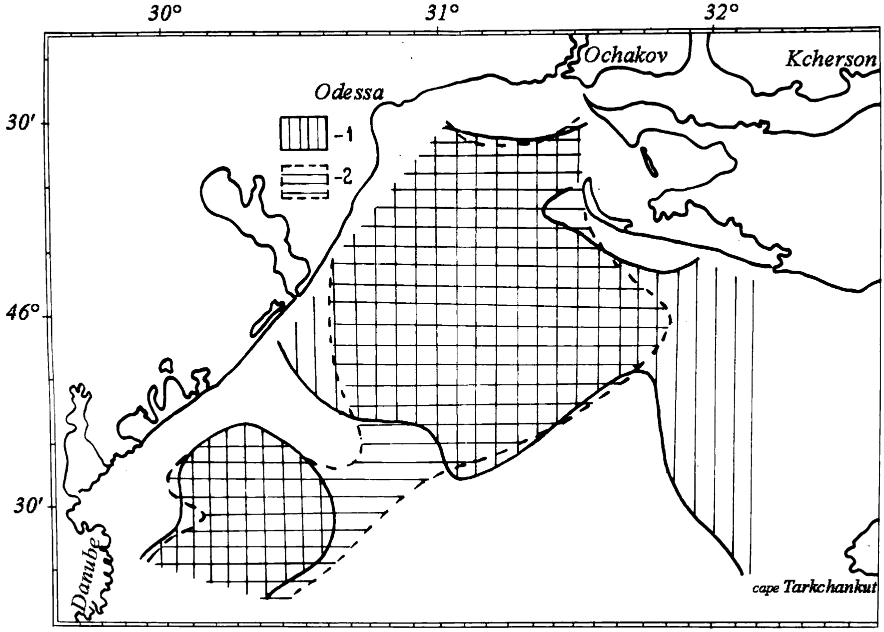


Fig. 4.7 Distribution of areas with suppressed vertical oxygen exchange, Ri > 10 (1) and zones of near-bottom hypoxia, $O_2 < 3$ mL/L (2) on the northwestern shelf of the Black Sea in August, 1979 (Fashchuk 1981)

Most often, water hypoxia was noted at vertical density difference of more than 2 conventional units per 1 m In such conditions, even after the N-NE storms with wind speed up to 15 m/s, the vertical density gradient was not broken, and aeration of deep layers did not occur (Photo 4.11).

4.3.2 Hydrochemical Characteristics

Compared with 1958–1959, by the beginning of the 1980s, the concentration of inorganic forms of phosphorus and nitrogen in waters of the northwestern Black Sea rivers have increased 5–7 times (Zaitsev et al. 1987), and in 1984–1989 in the Danube waters the content of total and ammonium nitrogen was 1.5 and 7 times higher than in 1980–1985 (Zaitsev 1992). As a result, from the beginning of the 1960s the positive trends in the content of inorganic forms of phosphorus (P_{min}), averaged 0.3–1.4 μg\L per year, with a maximum of 8 μg\L per year on the Danube offing, began to be noted on the northwestern shelf. The similar positive annual tendency of 0.2–0.8 μg\L was observed also in the open shelf areas (Selin et al. 1992). In the late 1980s, the average content of these compounds in shelf waters increased 2 times (Garkavaya et al. 1991; Selin et al. 1992). In the surface layer of the Dnieper and Danube areas the phosphate concentration increased

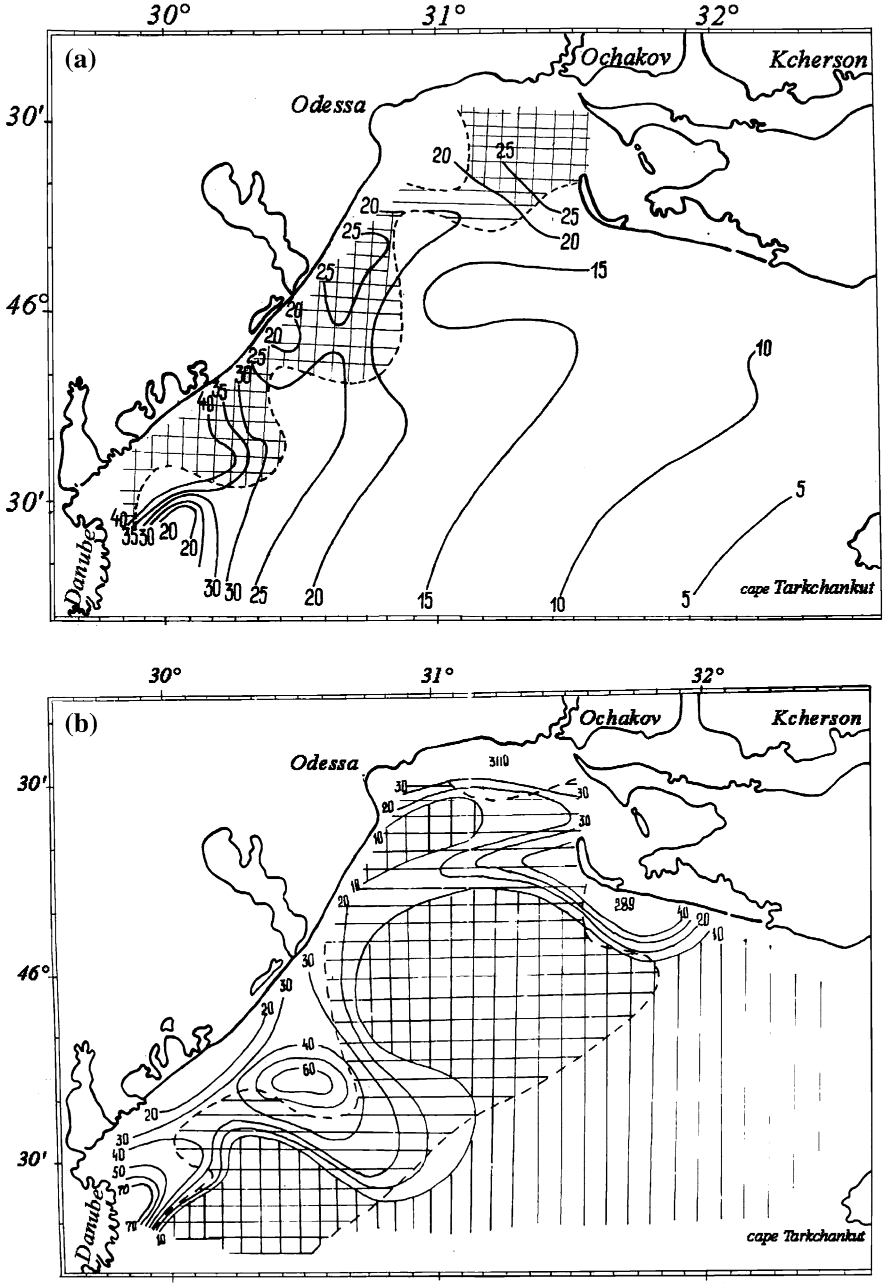


Fig. 4.8 Distribution of hypoxia zones (*dashed line* and *horizontal hatching*) and components of the Richardson number (*vertical hatching*) on the northwestern shelf in spring (**a**) and summer (**b**), 1979 (Fashchuk 1982) Isolines: in **a** vertical gradients of conventional density, $\times 10^2$; in **b** vertical gradients of current velocity, $\times 10^4$

Photo 4.11 In summer, because of high stability of the northwestern Black Sea shelf waters, at the sea depth of only 10 m even storms with force of 3–4-force cannot destroy vertical density gradient and ventilate the near-bottom water layer

by 30 and 15 μg\L, and in the bottom layer—by 40 and 10 μg\L, respectively. The nitrate content increased 4–6 times (Zaitsev et al. 1987), and the ammonium nitrogen concentrations rose from 27 to 350 μg\L in the surface layer and from 40 to 325 μg\L near bottom. In the hypoxia zones its content could reach 500–600, and even 900 μg\L (Garkavaya et al. 1991).

In 1991–1993, in the Russian zone of the Dnieper the presence of OCP in river waters was noted at 60–70% of stations in 20–25% of samples. At 37% of observation stations in 20% of samples the presence of trifluraline, with concentrations up to 0.183 μg\L, was registered. The maximum concentration of different OCP forms reached 0.113–0.44 μg\L (Korotova et al. 1998). In 2000, after the accident at the enterprise *PEMIN S.F.* (Baya-Bursa, Romania), in point of town of Reni on the Danube the content of Cu and Fe in river water made up 24 MAC, and that of Zn—5 MAC (Dyatlov and Petrosyan 2001; The Kiliyskaya 2001).

In 1978–1982, the content of P_{tot} and N_{tot} in the influence zone of the Danube waters, comprised 70–80 and 1,000–2,000 μg\L, respectively, exceeded more than hundredfold the similar values observed here in the early 1950s. By the end of the 1980 these values have increased 1.8 and 1.5 times more (Zenin and Zaitseva 1989). The content of organic nitrogen and phosphorus in waters of the

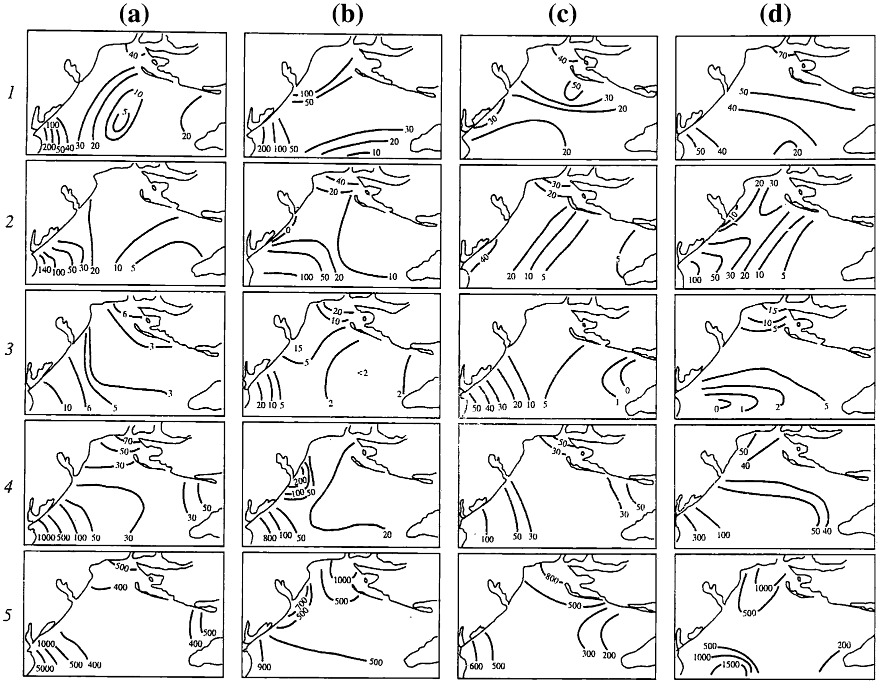


Fig. 4.9 Distribution of hydrochemical characteristics (μg\L) in spring (**a**, **b**) and summer (**c**, **d**) in the surface (**a**, **c**) and near-bottom (**b**, **d**) water layers of the northwestern Black Sea shelf (Zaitsev et al. 1985; *1*—PO_4^{-3}; *2*—P_{org},; *3*—NO_2^-; *4*—NO_3^-; *5*—N_{org})

northwestern shelf during this period also increased 2–3 times (Zaitsev et al. 1985), and at the surface it amounted to 5,000 and 140 μg\L in spring, and 800 and 40 μg\L in summer, respectively. In the near-bottom layer these values here were 1,000 and 100 μg\L in spring and 1,500 and 100 μg\L in summer (Fig. 4.9).

The natural result of increase in the pollution level of surface coastal sea waters with phosphorus and nitrogen compounds was the eutrophication (hyper-fertilization) of these areas of the sea resulted, in turn, in growth of its primary production level because of mass phytoplankton development. At present, the zones of maximum content of chlorophyll *a*, an indicator of intensity of this process, are located along the coast, from the Dnieper to the Dniester, and in the near-mouth areas of the Danube and off the coast of Romania they extend to the outer shelf (Fig. 4.10). According to this indicator, waters of the western Black Sea coast are classified as mesotrophic and eutrophic, and in the Danube influence zone they fall into a category of hypertrophic waters, as the content of chlorophyll *a* here exceeds 10 mg/m^3 (10 times higher than in the high sea) that is comparable with the most highly productive regions of the World Ocean (Practical Ecology… 1990).

Now, in the northwestern Black Sea the amount of dissolved organic matter has increased 4 times (Zaitsev 1992), and during summer it may vary from 15 to

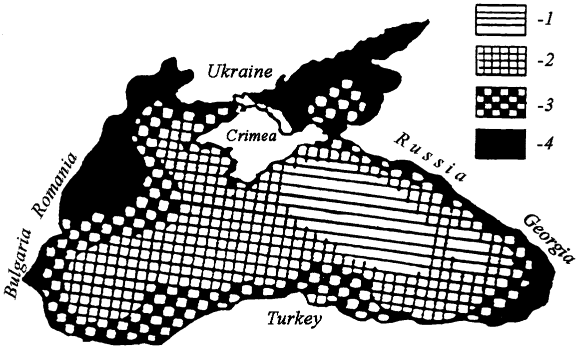


Fig. 4.10 Distribution of chlorophyll '*a*' on the Black Sea aquatory (*1*—0.4; *2*—0.7; *3*—1.0; *4*—10 mg/m^3; Practical Ecology… 1990)

50 mg/L (Fashchuk and Sebakh 1984). For the last 30 years in the whole water column of the Black Sea this indicator has increased by 6–8 kg/m^2 (Torgunova 1994).

In 1992–1993, on the Dnieper, in water of the Zaporizhia Reservoir the content of oil hydrocarbons was 3–10 mg/L (10–30 MAC). In the Dniprodzerzhynsk Reservoir this indicator exceeded MAC 1.5–2 times, and in the Kakhovka Reservoir, in the confluence of the Mokraya Moskovka River, their content was 100 times higher than norm (28–30 mg/L). The concentrations of heavy metals (Co, Cd, Ni, Pb, Mn, Fe) in waters of the Dnieper tributaries such as the Mokraya Sura, Samara, Orel Rivers, amounted to 1.5–3 MAC, those of oil hydrocarbons—up to 10 MAC (Dvoretsky et al. 2001; Shapoval and Kuklya 2001).

4.4 Tendencies in Changes of Hydrobiological Components of Shelf Ecosystem and Their Consequences

By the mid-1980s the intensification of primary production in the process of mass phytoplankton development in the hyper-fertilized surface water layer of the shelf has got the catastrophic character, and its consequences associated with the dying off of surplus organic matter and its destruction in the near-bottom layer, have contributed essentially to intensification of the summer hypoxia there.

4.4.1 Changes in Phytoplankton Populations

Within the last 20 years the phytoplankton biomass in the northwestern Black Sea has grown 26 times, and over the whole sea its concentrations have increased from 52 to 1,000 g/m^3 (Zaitsev 1992). With that, the share of diatomic algae in their total biomass reduced to 40%, while that of peridiniates (small-celled species) increased from 18.8 to 54.4%. In 1957, three areas of intensive phytoplankton development (blooming) were distinguished in the northwestern Black Sea.

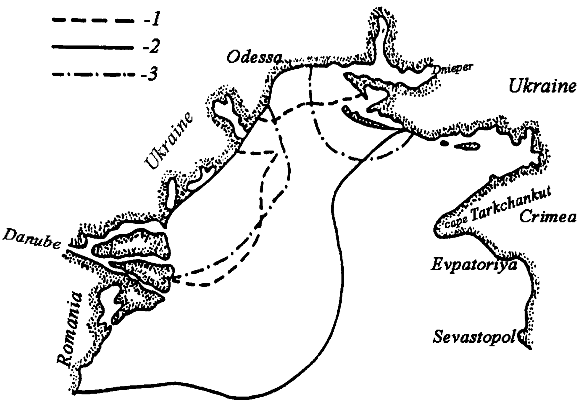


Fig. 4.11 Position of water "blooming" zones in the northwestern Black Sea (*1*—spring; *2*—summer; *3*—autumn (Nesterova 1987)

Now they have formed one extensive area occupying up to 50% of the shelf aquatory and 8–10 times exceeding them by size (Fig. 4.11; Nesterova 1987).

The scales and intensity of blooming increased considerably, having reached a level of the "red tide" phenomena, typical for the high-trophic regions of the World Ocean (Photo 4.12). The maximal abundance of peridiniates (*Exuviaella cordata*) during the periods of "red tides" in the northwestern Black Sea can reach now 224 million cells/L, compared with 33 million cells/L observed here during the episodic blooms in the 1950s (Nesterova 1987). The intensive development of this phytoplankton species occurs in parallel with growth of biomass of earlier not abundant blue-green algae—coccolithophora. In the mouth of the Dnieper-Bug Liman the continuous water blooming was caused by some species of their representatives, which in the 1950–1960 were not considered as stimulants of blooming.

Moreover, the "red tides" began to be noticed off the coasts of Bulgaria and Romania (see Photo 2.3, top; Bodenau and Uzurelu 1978), where abundance of peridiniates in these periods could reach 800 million cells/L, and their total biomass—1 kg/m^3. There, despite a decrease in the share of diatoms in the northwestern Black Sea phytoplankton structure, "red tides" caused by development of such representatives of these species as *Cerataulina bergonii* and *Stephanodiscus hantzschii* began to be observed in this area. The abundance of these algae reaches 6–40 million cells/L (Nesterova 1987). These phenomena regularly are repeated there at present time also (Terenko and Kurilov 2001).

Along the coast of Bulgaria, in the areas distant from mouths f the large rivers, the "red tides" developing by type of oceanic ones (in the zones of intensive upwelling) due to blooming of not algae but protozoal infusorians *Mesodinium rubrum*, capable of photosynthesis owing to their biological features, (Tumantseva 1985) began to be noticed from the early 1980s. In such cases the abundance and biomass of these organisms reach 4.6 million inds./L and 280 g/m^3 that 2 times exceeds the values observed, for example, off the coast of Peru during the development "the red tides" there in the periods of the El Nino events (Sorokin 1982). This fact evidences that eutrophication of the western Black Sea shelf waters occurs not only due to continental drainage (outwelling) but also as a result

Photo 4.12 "Red tides" off the Irish coast (*top*) and in the Bay of Biscay (*bottom*) [www.visibleearth.nasa.gov]

of intensification of upwelling—lifting of deep waters of the open basin, enriched with mineral salts, to the surface.

4.4.2 Changes in Zooplankton Populations

In parallel with growth of biomass and changes in phytoplankton structure, the similar events occur in zooplankton populations of the Black Sea also. From 1960 to 1981 its total biomass in the northwestern Black Sea has increased 10 times. In the 1980s abundance of jelly *Aurelia aurita* in the Black Sea was 300 times (!) higher than biomass of all fish species of the basin (Zaitsev and Polishchuk 1984). With that, a share of *Noctiluca miliaris Suriray* has increased from 40 to 80%, and its biomass has grown 15 times. At the same time, some species of forage zooplankton such as cladocerans, infraneustonic pantellids have ceased to be met here (Zaitsev et al. 1988).

Over the last 30 years of the XX century the mean biomass of common jelly *Aurelia aurita* (Photo 4.13, *top*) in the Black Sea increased from 1.38 to 12 g/m^3, its stock in wet weight—from 670 thousand t to 500–600 million t, and occurrence in catches of juvenile trawl—from 21 to 89%. Only that part of jelly stock which lived in the northwestern Black Sea (more than 40 million t) in the mid-1980s consumed daily up to 62% of daily production of forage zooplankton of the whole sea and to 5–7% of its biomass (Zaitsev et al. 1984; Shushkina and Arnautov 1985; Flint et al. 1989).

In 1982 ctenophore *Mnemiopsis leidyi* (see Photo 2.3, bottom), predatory pelagic jelly animal, endemic of the Atlantic coast of North America, was for the first time met off the Southern Coast of Crimea (Vinogradov et al. 1992). In 1987 г it distributed widely in the northwestern Black Sea, Bosporus area, and bays of the Caucasian coast. In autumn, 1988 its biomass in the open sea reached 1.5 kg/m^2, in summer 1989, the ctenophore stock was 1 billion t, and by 1990 it continued to increase. The mean invader biomass in the sea coastal areas during this period was 2.8–3.2 kg/m^2, with a maximum in the northwestern Black Sea of 4.6 kg/m^2. In the Gelendzhik—Anapa area and the near-Bosporus aquatory this value reached 11–12 kg/m^2. With that, the great bulk of ctenophore was concentrated in the upper top 15–20-m layer.

The ctenophore population with biomass of 1.5 kg/m^2 consumes 40% of biomass and 80% of zooplankton production. Moreover, it consumes larvae of mollusks, fishes, and jellyfish juveniles as food. The much larger, compared with jellyfishes, food competitiveness of new invader and its mass distribution in the Black Sea led to the fact that by 1989, in comparison with the period of 1978–1988, the jellyfish biomass reduced here from 400 to 60 million t, and the number of thermophilous forms of fodder zooplankton and arrow worms decreased 4.4 and 30 times, respectively. In addition, the carbon content in zooplankton decreased 2 times, to 0.2%, compared with 6%, characteristic, for example, for mesotrophic waters of the Pacific Ocean. The share of cold-loving fodder

Photo 4.13 Common jelly *Aurelia aurita* (*top*—[www.upload.wikimedia.org]) and root-mouthed jelly *Rhizostoma pulmo* (*bottom*—[www.photosight.ru]) are the typical representatives of Black Sea jellies

objects, calanus, living at depths of more than 50 m, increased in the total biomass of fodder zooplankton to 80% during this period.

In 1989–1990, the catastrophic decline of catches of summer-spawning pelagic fishes appearing in the zones of ctenophore development at the early ontogenetic stages, was noted in the Black Sea. In comparison with 1987, the Black Sea anchovy catches in the early 1990s dropped from 190,000 to 70,000 t, and those of jack—from 115 to 40 (in the eastern and northwestern sea, respectively) to 69,000 and 3,000 t. The similar decrease in kilka catches was observed in the Sea of Azov where this invader also obtained a wide distribution.

In 1991–1992 the *Mnemiopsis leidyi* biomass in the Black Sea reduced 3 times, compared with 1989–1990. In March-July 1992, г its stock was 4–16, in September–December—39, and in January–February, 1993—10 million t. By 2002,

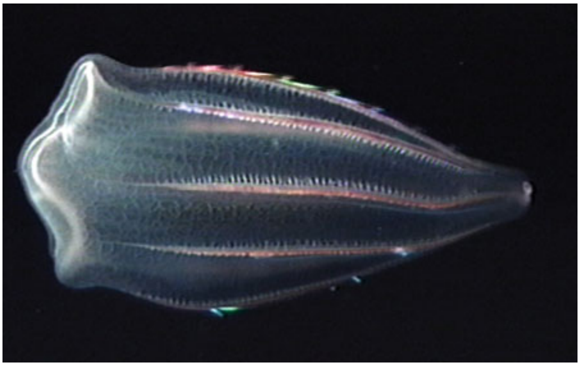


Photo 4.14 Ctenophore *Beroe ovata* [www.people.bu.edu]

after invasion of ctenophore *Beroe ovata* (Photo 4.14) feeding on *Mnemiopsis*, into the Black Sea in 1997, the abundance of predator *Mnemiopsis leidyi* has reduced sharply (Vinogradov et al. 2002).

4.4.3 Changes in Bacterioplankton Populations

In 1977–1978, the biomass of bacteria in the Black Sea during the summer season (maximum of development) increased 1.5–3 times, compared with the 1951–1967 period, and in 1989 its value 5 times exceeded the data for 1964. With that, the production of microorganisms grew 5–8 times. In the open areas of the sea it amounts to 20–60, and in coastal zone—to 100–200 mg/m^3 per day that in the latter case corresponds to the level of eutrophic waters. In the late 1970s the abundance of bacteria in the open sea areas during the summer period reached 300 thousand cells/L, and on the shelf this values reached 10 million cells/L (Sorokin and Avdeev 1991).

During the spring, 1984 in the eastern Black Sea the abundance of bacteria in the oxygen zone varied mainly from 50 to 300 thousand cells/mL, reaching in some cases 500,000 cells/L. The minimum values were noted in the open areas of the sea, and maxima—in the coastal zone. On the shoal of the western sea the concentrations of bacteria at that time reached 3–4 million cells/mL (Sazhin 1986).

In summer, 1986–1989, the value of this parameter in the various areas of the sea ranged from 700 to 800 thousand to 1 million cells/mL, with production fluctuating from mean (10–50) to maximal values of 150 mg/m^3 per day (Sazhin and Kopilov 1989).

By results of the more detailed investigations, during summer 1989 in the Caucasian coastal zone from Batumi to Anapa the total bacteria abundance in the 0–20 m layer varied from 60,000 to 3,050,000 cells/mL (areas of Novomikhailovka and Batumi–Anakliya, respectively). In the open Black Sea their content only in some samples exceeded 10^5 cells/mL, and off the coast of

Bulgaria this parameter ranged from 80,000 (on the Kamchiya River offing) to 500,000 cells/mL in the Burgas area (Mitskevich et al. 1992).

In the same time, according to the last mentioned authors, the abundance of saprophytic bacteria in coastal waters was at the upper limit of values fixed on the northwestern shelf in the late 1970s. In some cases it exceeded this level by a factor of 10–100. So, the highest abundance of heterotrophic saprophytic bacteria (to 700,000 cells/mL) was noted off the Cape Anakliya (Georgia) and in the Burgas Bay area (62,000 cells/mL). In the upper 10-m layer off Adler and Utrish it amounted to 40,000–60,000 cells/mL, and near settlements of Golovinka, Gudauta, Novomikhailovka and in the Sudak, Gelendzhik, Anapa bays—200—9,000 cells/mL.

At the end of the XX century 1 liter of water from the Odessa Bay (Photo 4.15) contained hundreds thousand cells of coliform bacillus *Esherichia coli*, at the allowable limit of 1,000 cells/L. Apart from this bacillus, salmonella, Shigella, cholera vibrio, viruses, helminth ova, and other pathogenic organisms were found at that time in water and bottom sediments of the bay. In 1995, the adverse epidemiological situation with cholera has developed in Mykolaiv at the Bug Liman, and the Odessa beaches were periodically closed for swimming by the unsatisfactory sanitary indications (Zaitsev 1998).

According to the data obtained by specialists from the Institute of Global Climate and Ecology of the Russian Academy of Sciences, in September, 1992 in coastal waters of the Black Sea from Odessa to Batumi the maximal abundance of heterotrophic saprophytic bacteria (0.5–9 million cells/mL) was noted in the areas of Tuapse and Batumi. In the northwestern Black Sea this indicator varied from

Photo 4.15 By the 1990s the Odessa Bay has become a storage reservoir for waste products of the city population and its industrial plants (Photo from ISS)

tens to hundreds thousand cells in 1 mL of water mL, and along the Crimea, from Yalta to the Kerch Strait—from 5,000 to 50,000 cells/mL (Review… 1993). As a result of late changes, the sanitary-bacteriological conditions in the Black Sea were as the following:

- by the index of lactose-positive Bacillus coli, in 1995, the situation in the sea of the Novorossisk area was characterized as "crisis" (240,000 cells/L), and at the beaches of Sochi and Gelendzhik in some samples—close to "crisis";
- the biomass of bacteria in the Black Sea during the summer season (development maximum), 1977–1978 increased 1.5–3 times, compared with the period of 1951–1967, and in 1989 this indicator exceeded the data for 1964 by a factor of 5. In the late 1970s the abundance of bacteria in the open sea areas during the summer period corresponded to the "catastrophic" situation (>10,000 cells/mL). The similar situation continued in the various coastal areas of the sea from Bulgaria to Georgia in the late 1980s;
- by abundance of heterotrophic saprophytic bacteria, the conditions at the beaches of Georgia were "catastrophic" (to 700 thousand cells/mL); in the Burgas Bay (Bulgaria) and at the coast of Sochi—Adler—"crisis" (40–60 thousand cells/mL), and in the areas of Sukhumi, Gelendzhik, Anapa, Kerch Strait, Sudak—"rather satisfactory".

4.5 The Prime Causes of Intensification of Summer Ecological Crises on the NW Shelf of the Black Sea

For the appearance, development and maintenance of anaerobic conditions in marine ecosystems it is necessary that the rate of oxygen consumption would exceed the rate of its flux into the near-bottom layer. It occurs at weakening of deep water aeration in the process of vertical oxygen exchange O_2 (physiodynamic mechanism) and photosynthesis (biochemical mechanism), and under the intensification of oxygen consumption for destruction of organic matter (biochemical mechanism).

The facts given in Sects. 4.3–4.4 indicate that by the mid-1970s the hydrological and hydrobiological conditions of marine environment on the northwestern shelf environment essentially changed. Therewith, the specified main natural mechanisms regulating the oxygen balance in the near-bottom, began to "work" in such a manner that its receipts part reduced, while the consuming part increased. So, the intensity of hydrophysical processes (vertical mixing) and photosynthesis process in the near-bottom layer determining the aeration of water column decreased, while the biochemical mechanisms regulating the rate of oxygen consumption in the near-bottom layer became much more active.

After studying of the natural and anthropogenic factors determining the intensity of hydrophysical and biochemical processes in the coastal marine ecosystem, the scheme of changes in components of the oxygen balance in the near-bottom layer, leading to appearance and development of the crisis events in the northwestern Black Sea has been developed.

4.5.1 The Causes of Hydrological Structure Transformation

For coastal waters of the Black Sea the river runoff as a factor affecting their hydrological, hydrochemical and biological structure, has the determining value. Until the mid-1950s the anthropogenic withdrawal of river drainage almost did not affect the Black Sea ecosystem state. Since this period the irretrievable water consumptive for needs of national economy began to increase by 0.74 km^3 annually, and by 1986 it reached 30 km^3/year (Nikolenko and Reshetnikov 1991). From them, the one third falls on the Danube and 50%—on the Dnieper waters. Until 1950 the amplitude of fluctuations of river discharge withdrawal did not exceed 5 km^3/year, and now it makes 14 km^3/year. The fluctuations of the total runoff by reason of natural changes in water content of the rivers from 1960 to 1980 made 75–80% of its mean volume (340.6 km^3/year; Kuksa 1994). The period of growth of anthropogenic withdrawal of river drainage coincides with the stage of increase in water content (1946–1986), when the natural drainage into the Black Sea increased annually by 2.9 km^3. Thus, the rate of natural increase in the fresh water inflow to the Black Sea exceeds 4 times its anthropogenic reduction which volume (15% of the total drainage) is compensated completely by natural factors.

At the same time, as a result of regulation of the river drainage, for the last 30 years its supply to the Black Sea in summer decreased 2.5 times (Timoshchuk 1977; Altman et al. 1988). The consequence of its intraaanual transformation appears as the spreading of saline sea waters in the near-bottom layer from the open shelf into the near-mouth zones, river mouths, estuaries and limans (The Dniester-Bug … 1989; Samoilenko 1990). Now sea waters are fixed even in the Kherson area (Timoshchuk 1977). Based on such analysis, the physico-dynamic mechanism of suppression of vertical shelf water mixing and weakening of ventilation of the near-bottom layer seems as the follows (Fig. 4.12):

1. Prior to the beginning of intensive economic activity, the freshening of surface water layer in the process of spring high water resulted in natural transformation of a pycnocline layer "from above" that led to sharpening of vertical gradients of this characteristic (Fig. 4.12a).
2. In years with severe winters (intensive cooling and large pool of cold waters in the near-bottom layer by summer), warm spring (intensive warming of the surface water), and low wind weather in summer (weakened water mixing), the vertical oxygen exchange on the shelf aquatory after floods was suppressed (black-and-white arrow in Fig. 4.12a). The probability of such event in years with the big floods is higher than in the normal and shallow years.
3. As a result, under the developed physico-dynamic conditions in the northwestern Black Sea, adverse for oxygen exchange, as well as in many other earlier

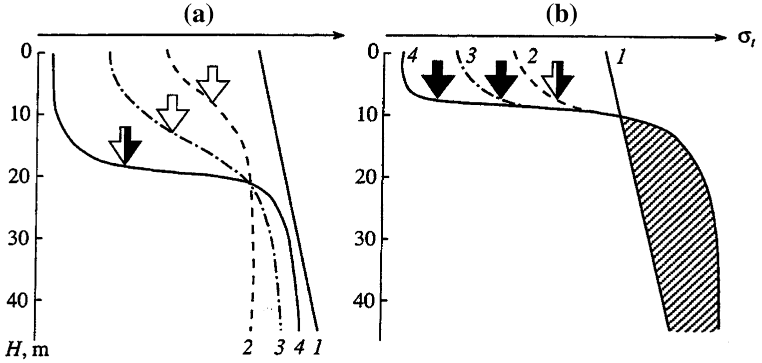


Fig. 4.12 The vertical distribution of conventional density of the northwestern shelf waters, schematizing the hypoxia development prior to (**a**) and after (**b**) intensification of economic activity in the watershed territory (Fashchuk 1995): *1*—Mean annual distribution; *2*—summer distribution in years with low water content; *3*—the same but for years with normal water content; *4*—the same but in years with high water content The *black*, *black-and-white*, and *white arrows* denote the constantly suppressed, periodically suppressed, and favorable oxygen exchange, respectively. *Hatching* shows the advection of saline water and hypoxia in the near-bottom layer

mentioned, even non-eutrophicated regions of the World Ocean, such as the Cariaco Basin, the Australian Cabbage Tree Basin, intermediate depths of the Arabian Sea and deep-sea areas of the World Ocean, the water hypoxia is formed in the process of natural destruction of organic matter without oxygen access.

Thus, prior to intensification of economic activity (regulation of river drainage), the episodic oxygen deficit in the near-bottom benthonic layer of the area under investigation was associated with a combination of natural climatic processes, such as water content of the rivers, severity of winters, rate of the spring-summer warming and wind regime over the aquatory during the summer period, and the organic matter content and rates of its destruction under the natural conditions are always sufficient for the water hypoxia development below the pycnocline in the absence of oxygen access here.

After the regulation of the river drainage the natural *physico-dynamic mechanisms* of anaerobic zone formation were added with two processes determined the intensification of hypoxia phenomenon. They included the advection of saline waters in the near-bottom layer into the near-mouth shelf areas and lessening of discharge currents (Fig. 4.12b).

1. The former mechanism determined the transformation (sharpening of vertical density gradients) of pycnocline “from below” (hatching in Fig. 4.12b), and the latter- the formation of stagnant zones on the shelf with weak shear of currents.
2. Together with the earlier observed natural transformation of the density gradient layer in the flood period, the ecological effect of the mechanisms added by the anthropogenic reasons is manifested today in cease of the near-bottom layer ventilation not only at the coincidence of natural factors but almost annually (black arrows in Fig. 4.12b).

3. One of the proofs of adequacy of the suggested mechanism of water hypoxia intensification is the fact that by the results of field observations (Zaitsev 1992, Fashchuk 1995), in 1986–1987 (the beginning of the period of climatic decrease in water content) this phenomenon occupied much smaller area of the northwestern Black Sea than during the period of high water content continued until the mid-1980s.

4.5.2 The Causes of Hydrobiological Structure Transformation

The formation of water reservoirs on the main Black Sea rivers (their number on the Danube is about 20, and on the Dnieper there are 7 large and more than 250 thousand small reservoirs located in the river basin) determined the fact that inorganic compounds of phosphorus and nitrogen began to be consumed intensively on their aquatories. Water in the reservoirs has "bloomed", and, hence, the considerable amount of phosphorus is transported now into the sea as a part of organic compounds. The similar changes occurred with nitrogen also—the content of organic and ammonium nitrogen in shelf waters increased. But the most important thing is the considerable (5–12 times) increase in the amount of organic carbon carried by the rivers into the sea (Photo 4.16).

Photo 4.16 In summer reservoirs of the Volga cascade "bloom" as intensively as the Dnieper reservoirs (Blooming of the Volgograd Reservoir in the confluence area of the Akhtuba River, Photo from ISS)

The content of organic carbon in the upper 50-m layer of the sea increased from 2–3 to 8–12 mgC/L. Correspondingly, there was a sharp growth of organic phosphorus and nitrogen concentrations (to 1–1.2 and 11–25 μg-at/L). In the northwestern sea, especially in the near-mouth areas, these values increase tenfold and more. In 1988–1991, in the zone of the Black Sea shelf the content of ammonium nitrogen rose considerably (to 2.2 μg-at/L), though in the deep-water (open) sea its concentration in the surface layer practically did not change (0.2–0.4 μg-at/L). At that time in the coastal shallow zone of the sea the very high urea concentrations (up to 11–19 μg-at/L) were fixed (Sapozhnikov 1992).

At the same time, the qualitative composition of river drainage has changed essentially as a result of economic activity in the watershed areas. For example, from 1963 to 1972 the application of nitrogen and phosphorus fertilizers on the watershed of the Dnieper increased 6 and 3 times, respectively (Denisova et al. 1974). The anthropogenic eutrophication of river waters resulted in an increase in the content of nitrates and phosphates in them during 1977–1983 6 and 3 times for the Danube, 1.5 and 5.5 times for the Dnieper, and 6 and 6.5 times for the Dniester, compared with 1948–1959 (Zaitsev et al. 1987). For 1980–1990 the total nitrogen supply with waters of the Danube and Dnieper increased 8 times; the input of phosphates with waters of the Danube—10 times, and with waters of the Dniester—2 times (Zenin and Zaitseva 1989; Fashchuk et al. 1995).

The changes in chemical water composition in the coastal zone of the Black Sea have been accompanied by alteration in the structure of its phyto- and zooplanktonic communities. Allochthonous organic matter favored the rapid development of bacterial microflora, fungi, and protozoa that, in turn, accelerated considerably the nutrient recycling and increased the primary production of organic matter (Fashchuk and Sapozhnikov 1999). It is the intensification of production—destruction processes that resulted in mass development of short-lived species, such as Noctiluca, jellyfishes, ctenophore. The stable equilibrium of the Black Sea ecosystem was broken, and it turned out to be in a transitional state.

The intensive development of production-destruction processes in the Black Sea is confirmed by the fixed high activity of enzymes (hydrolyst, alkaline phosphatase, nucleoprotease, and electron transport chain), responsible for various types of organic matter transformation (Agatova et al. 1989). The acceleration of turnover of organic matter and nutrients in the production—destruction cycle of coastal waters has caused the appearance of "red tides", powerful blooming of *Exuviaella cordata*, *Goniaulax Poliedra*, *Goniaulax Poligramma*, and mass development of such infusorians as *Mezodinium rubrum*. All these signs of eutrophication appear not only in time when the large amount of phosphorus, nitrates and silicium are accumulated in water, as it was noted in the Varna Bay (23.5, 273, and 62.3 μg-at/L, respectively) and not when the water contains the considerable amount of organic matter (mouth zone of the Dnieper) but only under the intensive development of microheterotrophs and very high rate of the production—destruction processes (Sapozhnikov 1992).

During the period of "red tide" (blooming of *Goniaulax Poliedra*) off the coast of Bulgaria in the summer 1989 the participants of expedition conducted by

VNIRO on board R/V *Akademik Knipovich* have observed a decrease in concentration of the dissolved organic matter in the zone of phenomenon development to 6.5 mgC/L, while the content of suspended organic carbon has increased 2–3 times, to 3.5 mgC/L. The inorganic forms of nutrients were depleted completely but the content of organic phosphorus increased to 23 μg-at/L, that of organic nitrogen—to 681 μg-at/L. The primary production in the "red tide" zone reached 1.5 g/m^3 per day. The chlorophyll *a* concentration in the phenomenon development area equaled 106 mg/m^3. With that, the pigment index of phytoplankton was not high (1.84) that indicated a good physiological condition of algae and their sufficient supplying with inorganic nutrients (Sapozhnikov 1992).

The consequence of "red tides" was associated with accumulation of surplus amount of organic matter (OM) formed after dying off of algae participated in blooming, in the near-bottom layer. This, in turn, resulted in an *increase in rate of oxidation of surplus organic matter* in the near-bottom layer 3–4 times, in comparison with its background value (Fashchuk and Sebakh 1984). The values of BOD-5 here reached 2–4 mgO_2/L, and the constants of OM oxidation rate 3–5 times exceeded values, characteristic for the open sea. The degree of mineralization of decomposable organic matter was 60–70% for 5 days that was 5 times higher than in the near-Bosporus area and, for example, in the Ionian sea.

The investigations conducted in the 1990s confirmed our results obtained in the mid-1980s. According to these data, the values of BOD-5 in the northwestern Black Sea during the spring-autumn period may reach 3.56–5.80 mgO_2/L, and permanganate value (indicator of intensity of OM destruction)—5.27 mgO_2/L (Savin and Podplyotnaya 1991).

4.5.3 The Complex Mechanism of Suffocation Events Intensification

The analysis made enables to conclude that deterioration of oxygen regime in the near-bottom water layer of the northwestern Black Sea during the summer period and development of seasonal zones with hypoxia and anaerobic conditions, started from the mid-1970s is a complex phenomenon. Its prime causes were associated with *hydraulic engineering on the main regional rivers (Danube, Dnieper, Dniester) and change in hydrochemistry of river waters as a result of transformation of their qualitative composition in the ecosystems of reservoirs and chemization of agriculture in the watershed basin.*

1. Building of water reservoirs, regulation and, as consequence, intraannual redistribution of river drainage, has determined a seasonal change in physico-dynamic structure of waters in the area, manifested in strengthening of water stratification here and weakening of vertical shear of currents. As the result, in contrast to the 1930s–1950s, in the spring-summer period the vertical turbulent oxygen exchange on the northwestern shelf aquatory is suppressed not episodically (in years abounding in water with sever winters and early spring with low wind weather) but almost annually.

This became a "trigger" for formation of hypoxia in the near-bottom layer. At the final stage of this process the above-mentioned conditions (absence of aeration) lead to formation of hydrogen sulfide in water as a result of sulfate reducing bacteria activity in anaerobic environment, and development of suffocations on the shelf. Nevertheless, the specified anthropogenic factor and physico-dynamic mechanism triggered by it are not unique factors determined the intensification of ecological crises.

2. On the vast aquatories of reservoirs a natural transformation of natural river drainage occurs, with the intensive consumption of inorganic compounds of phosphorus and nitrogen in the process of phytoplankton development (blooming). As a result, the rivers began to carry these elements into the sea (at periodic releases from reservoirs) mainly as a part of organic compounds. Moreover, the amount of organic carbon in river drainage, a product of algae died off after blooming in reservoir, has increased also.

Allochthonous organic matter in the near-mouth sea areas favors the development of bacterial microflora and protozoa that has intensified the nutrient recycling (natural eutrophication) after their dye-off and process of subsequent primary production of organic matter. This, in turn, caused the mass development of short-lived zooplankton species, such as Noctiluca, jellyfishes, ctenophore. It is those species that are the main consumers of organic matter formed not from "new" mineral compounds of phosphorus and nitrogen but from nutrients composed in the process of recycling from the secondary organic matter carried out from reservoirs.

3. Along with the above-considered process, the similar result, eutrophication of sea waters, may be reached through the direct pollution of the rivers by inorganic compounds of nitrogen and phosphorus (fertilizers) washed away from soils of farmlands or appeared in the rivers because of their negligent storage and application. Its result is a development of "red tides" on the shelf aquatory and secondary pollution of the sea bottom after dye—off of blooming algae.

In the process of secondary pollution in water column of the northwestern Black Sea the significant amount of suspended matter (seston) is formed also, reducing transparency of waters in the photic layer of the open shelf during the summer period 1.5–2 times, and in the coastal zone—5–10 times. Moreover, sinking particles of died off phytoplankton ("sea snow"), concentrating on the boundary of pycnocline layer (depths of 5–7 m), isolate the near-bottom layer from sunlight penetration almost completely, reducing its light conditions below pycnocline. As a result, the depth of the photosynthesis lower boundary decreases, and *the process of oxygen production in the near-bottom layer appears almost suppressed* (Zaitsev et al. 1987).

4. Thus, in parallel with deterioration of aeration under the influence of physiodynamic mechanisms and due to suppression of photosynthesis in the low light conditions, the natural and anthropogenic eutrophication has resulted in an intensification of biochemical mechanisms of oxygen consumption in the near-bottom water layer of the shelf. For this reason the oxygen deficit began to be formed here much faster, to continue longer, to appear in years with short stagnation of waters, independent on coincidence of climatic factors which can only aggravate or weaken this process in the time or space scales.

Photo 4.17 "Dead" gobies picked up in time after suffocation do not contain toxins and are serviceable enough for cooking of famous Black Sea delicacy (photo by author)

Taking into account the irreversibility of the considered anthropogenic processes now, it is reasonable to assume that their final ecological consequences, suffocation events (kill of bottom inhabitants during the summer period), will continue in the near future, intensifying in wet periods and weakening during the normal and dry years, and scales of the crises will be determined by hydrometeorological conditions of the year (Photo 4.17).

We made this forecast in 1981 (Fashchuk 1982) and, unfortunately, it is justified up to now. Until the mid-1980s (wet period) suffocations covered annually the larger aquatory of the shelf. From 1986 to 1987 (the beginning of dry climatic period) the areas of development of ecological crises reduced essentially. From the early 1990s this phenomenon has taken on the character of catastrophes again, repeating almost regularly (including 2000–2003) in summer on the shoal of the northwestern Black Sea (Garkavaya et al. 2000; Khutorny 2001; Berlinsky et al. 2001, 2003, 2004; Tuchkovenko and Dotsenko 2003).

4.6 Mathematical Modeling of the Anaerobic Zone Dynamics and Timing of its Existence on the Shelf

The long-term monitoring of suffocation events has allowed to conclude that amplitude of interannual fluctuations in dimensions of shelf areas with water hypoxia in the late summer varies, depending on the volumes of the Danube and Dniester runoffs in June-July and May–June, respectively. For the Dnieper it was impossible to identify such characteristic months (Berlinsky and Dykhanov 1991). Water hypoxia in the Danube near-mouth area continues until September, with the Danube runoff volume in June-July of 70 km^3. For the central shelf areas the similar conditions are provided under the Dniester runoff in May–June of 4 km^3. The correlation coefficient between parameters under consideration is 0.65, with the 95% significance level. By results of the long-term observations the statistically significant relationship between the near-bottom oxygen concentration in August off Odessa and total inflow of organic matter with Dnieper waters in July–August was revealed also (Kovalchuk 1986).

4.6.1 Spatiotemporal Dynamics Under the Influence of Hydrometeorological Factors

The investigations of shelf anaerobic zone dynamics by means of the *Ecoshelf* program system enabled to reveal the dependence of hydrosulfide zone dimensions on indicators of the river runoff pollution and biochemical parameters of shelf waters, including zooplankton mortality, phytoplankton production, rates of detritus formation and oxygen consumption for organic matter oxidation, amount of hydrogen sulfide production under anaerobic conditions (Belyaev and Konduforova 1990). Moreover, the significant role of currents and horizontal turbulent exchange in distribution of phyto- and zooplankton, organic matter and nutrients participating in the anaerobic zone formation indirectly, was also established:

- under strong northeast winds the Danube waters are driven to the Romanian coast and practically do not spread into the open central shelf areas;
- under low wind weather (most typical conditions for anaerobic zone development) on the anticyclonic circulation is developed on the shelf aquatory, encouraging penetration of the Danube waters to the 200-km distance in the central northwestern shelf;
- this results in a hundredfold increase in organic matter concentration, decrease in water transparency and, correspondingly, intensity of photosynthesis;
- under winds of intermediate force (to 5 m/s) the account of density stratification (baroclinicity) in calculations does not affect essentially the spatial distribution of anaerobic zone, which in this case depends only on wind force;
- model enhancement of the coefficient of horizontal matter exchange from 10^5 to 10^7 cm^2/s shows the enlargement of the area from the Danube of spreading of phosphorus and organic matter compounds 3 times, and for nitrogen—6 times;
- under the similar enhancement of the coefficient of horizontal exchange within the constant distance from the Danube mouth, the content of nitrogen increases 10 times, and that of phosphates and organic matter—100 times.

4.6.2 Chemical Dynamics

Stability of the anaerobic zone depends on the intensity of processes of oxidation and formation of hydrogen sulfide, rate of mass transfer and variability of O_2 and H_2S concentrations in the zone of their interaction at interface of aerobic and anaerobic conditions, i.e., in the layer of coexistence of these reagents (C-layer). The results of investigations of chemical dynamics of hydrogen sulfide zone on the northwestern shelf (Selin et al. 1988) by means of the simulation model of oxidative sulfur transformation (Leonov and Aizatulin 1987b, 1995), with input data obtained at daily station in the anaerobic zone on the northwestern shelf, 8–9 September 1983 (see Sect. 4.1.2), in many respects confirmed the conclusions obtained with use of the *Ecoshelf* model system.

In the chemicodynamic context, the zone proved to be very responsive to alteration in synoptic situation. Slight short-term intensification of wind at daily station (up to 6 m/s within 4 h) resulted in a fivefold increase in the coefficient of vertical exchange, a 50-fold strengthening of reagent flow into the C-layer, and a 2.5-fold increase in its thickness. In this case, the rate of hydrogen sulfide oxidation increased due to growth of O_2 and H_2S concentrations in this zone in almost 20, rate of nitrification—in 5.3, and rate of oxygen consumption—in 14 times. The restoration of oxidation–reduction regime of the C-layer occurred in 4 h after cessation of wind action.

The rate of sulfate reduction in the near-bottom layer of the northwestern Black Sea shelf was not determined experimentally. Model calculations for calm weather showed that it equaled 0.45 mg-at S/(m^2h). Under these conditions, the time of existence of hydrogen sulfide zone in September, 1983, at the hypothetical retention of wind regime and wind speed of 6 m/s, was 70 h, i.e., almost 3 days.

The use of the model of chemical dynamics of the shallow anaerobic zone for other regions of the World ocean (Baltic Sea, Cariaco Basin) allowed to establish a common law for them (Selin et al. 1992):

- integral rates of hydrogen sulfide oxidation and oxygen consumption in the layer of their coexistence at the anaerobic zone boundary *are proportional to the ratio of average effective coefficient of vertical exchange to the C-layer thickness to the power of 1.2*.

The similar regularity is extended over all anaerobic basins, despite the fact that the C-layer thickness in them can vary from 2 to 200 m; temperature—from 3 to 21°C; salinity—from 11 to 35‰; and pH values—from 7 to 8.1. Thus, the dependences obtained allow to assess chemicodynamic activity of hydrogen sulfide zones, and to define, in combination with hydrometeorological forecasts, their state and development trends.

4.7 Experimental Study of the Shelf Anaerobic Zone Synoptic Variability for the Purpose of Natural Resources Rational Exploitation

The conclusions about irreversibility of processes of regulation and eutrophication of river drainage and, consequently, the continuation of development of near-bottom hypoxia and hydrogen sulfide contamination on the northwestern shelf during the summer period in the coming years do not exclude necessity to continue here, in the coastal zone off the Island Dolgy, separating the Egorlytsk Bay from the Tendra Bay such traditional types of economic activities as artificial cultivation of mussels on aquacultural plantations.

By the beginning of the 1990s the efficiency of this process decreased sharply, as, appearing in the anaerobic conditions, the most part of the mollusks attached to the special 3–5-m bearers—collectors vertically strung at depths of 5–10 m (Photo 4.18), perish and fall onto the bottom (Photo 4.19). Usually such events are observed in August, after stormy winds of the northern quarter.

4.7.1 Synoptic Variability of the H_2S-Boundary Position at the Different Hydrological Conditions

During the observations at the multiday station in the Tendra Bay (July 28–September 14, 1980), the upper 5-m water layer was almost homogeneous; therefore, the data corresponding to depths of 5 m and lower are included in the summary table of results (Table 4.1). During observations, three cases of wing strengthening to stormy (on August 10–11, 18–19, and September 12–13) were registered.

1. Stormy northwest wind on August 10–11 continued for 15 h. The vertical gradients of temperature, salinity and conventional density at the station during

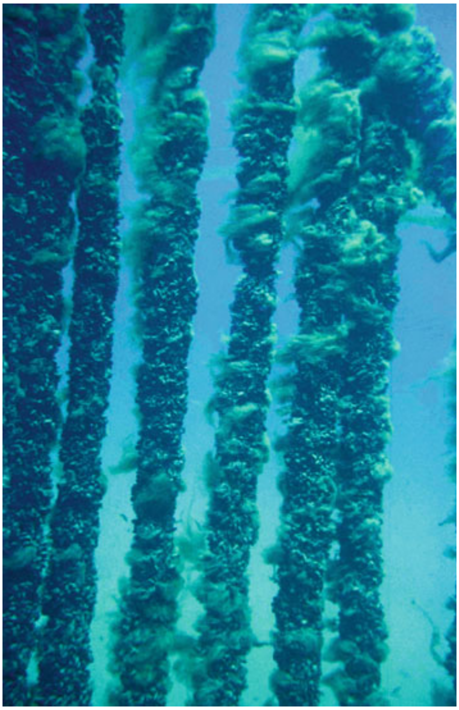


Photo 4.18 Mussel collectors with cultivated mollusks under favorable conditions (Photo by M. Pereladov)

Photo 4.19 The lower part of mussel collector from artificial plantation after "hydrogen sulfide bath" (Photo by O. Kudinsky)

that time made up 9.6°C, 5.68‰ and 6.44 of conventional density units per meter; the vertical oxygen exchange was suppressed (Ri > 10), in the near-bottom layer at depths of 7–8 m oxygen was not available, and hydrogen sulfide was noted organoleptically in samples of near-bottom water.

10 h after the beginning of wind with speed of 12–15 m/s, the oxygen concentration at depth of 7 m increased to 1.38 mL/L, salinity reduced from 16.90 to 13.47‰, temperature increased from 14.48 to 23.36°C, and aeration of the near-bottom water layer commenced (see Table 4.1). However, after the cessation of wind, this process was stopped in 15 h by advection of relatively cold, saline waters saturated with hydrogen sulfide from the open shelf areas (depths of 15–20 m), where hypoxia and hydrogen sulfide zone occupied 66% of the aquatory area at that time (see Fig. 4.4). As a result, at 2 a.m. on August 11, salinity at depth of 7 m increased to 16.06‰, water temperature dropped to 16.16°C, and the oxygen content decreased to zero value again. By 06:00 a.m. on August 14, in the process of continuing advection provoked by stormy offshore wind, water temperature at depth of 7 m fell to 13.98°C, salinity increased to 17.22‰, and oxygen content went down to zero value also at depth of 6 m. Thus, the upper boundary of water hypoxia at the station rose to depth of 5 m (by 2 m), and the oxygen concentration reduced here after the storm from 5.55 to 0.65 mL/L (see Table 4.1; Fig. 4.13 top B).

2. Such a situation was repeated under similar hydrological conditions on August 18–19. The regime restored within the preceding three-day period of

Table 4.1 The results of observations at multiday stations in the Tendrovskii Bay during storm wind in 1980 at depths of 4–9 m (dash means absence of data)

Date	Time	Wind		Current[a]		T (°C)					S (‰)					σ_r					O_2 (mL/L)				
		Direction (°)	Velocity (m/s)	Direction (°)	Velocity (cm/s)	4	5	6	7	8	4	5	6	7	8	4	5	6	7	8	4	5	6	7	8
10.VIII	10:00	310	12	168	03	24.12	24.20	–	–	14.21	10.29	10.80	–	–	15.93	5.08	5.42	–	–	11.53	5.23	4.78	–	–	0.00
	11:00	310	12	190	30	24.14	24.22	–	–	17.58	10.34	10.34	–	–	14.18	5.10	5.08	–	–	9.54	5.46	5.57	–	–	0.61
	12:00	310	12	150	31	24.32	24.30	24.12	14.48	14.24	10.35	10.49	11.22	16.90	16.90	5.05	5.15	5.76	12.20	12.24	5.53	5.39	4.22	0.00	0.00
	14:00	310	15	130	29	24.24	24.38	24.01	17.07	14.04	10.77	10.56	11.49	16.09	17.10	5.40	5.22	6.00	11.08	12.44	4.85	5.22	4.05	0.00	0.00
	16:00	310	10	176	36	24.24	24.04	22.02	15.76	14.66	10.59	11.78	14.43	16.83	16.83	5.26	6.19	6.43	11.75	12.12	5.14	4.27	0.00	0.00	0.00
	18:00	310	08	200	37	24.20	23.69	23.08	16.82	14.39	10.89	12.56	13.72	16.22	16.39	5.49	6.85	7.90	11.24	12.19	5.07	3.44	0.51	0.00	0.00
	20:00	310	05	164	31	24.34	24.08	23.68	22.99	15.26	10.17	11.88	12.86	13.88	16.68	4.92	6.25	7.09	8.05	11.88	5.77	4.53	3.52	0.31	0.00
	22:00	340	12	190	35	24.24	24.19	23.61	23.36	15.90	10.97	12.05	12.94	13.47	16.49	5.55	6.38	7.18	7.63	11.63	4.84	4.51	3.27	1.38	0.00
11.VIII	2:00	360	10	160	32	24.24	24.03	23.52	16.16	14.77	10.49	12.72	12.99	16.05	16.96	5.20	6.90	7.24	11.24	12.19	4.96	3.99	3.28	0.00	0.00
	6:00	360	05	46	27	23.83	23.52	22.56	16.56	15.12	12.23	12.73	13.40	16.37	16.66	6.59	7.05	7.90	11.90	11.90	4.10	3.79	2.11	0.00	0.00
	10:00	310	02	237	24	23.99	23.41	24.91	19.44	16.26	11.10	11.42	13.10	15.23	16.41	5.70	6.09	7.09	9.94	11.48	4.68	4.48	3.34	0.00	0.00
	14:00	290	02	304	20	23.94	23.72	23.38	18.62	15.52	11.41	12.07	13.23	15.67	16.29	5.94	6.50	7.45	10.44	11.55	4.16	4.13	2.69	0.00	0.00
12.VIII	6:00	20	03	160	20	23.22	23.32	17.34	14.01	13.66	11.27	12.94	15.83	17.14	17.25	6.02	7.25	10.84	12.48	12.62	4.68	2.89	0.47	0.00	0.00
13.VIII	10:00	120	03	160	16	23.30	20.46	14.84	14.00	13.22	12.25	14.19	17.09	17.17	15.58	6.93	8.90	12.28	12.50	11.43	3.78	1.26	0.00	0.00	0.06
	18:00	225	03	70	08	23.24	20.81	15.00	13.76	13.15	11.99	13.11	16.95	17.30	16.19	6.32	8.02	11.50	12.65	11.90	4.14	1.61	0.00	0.06	0.21
14.VIII	6:00	130	02	250	14	22.48	21.89	15.69	13.98	13.44	12.29	14.02	16.71	17.22	16.53	6.97	8.42	11.83	12.54	12.12	3.46	0.65	0.00	0.00	0.13
15.VIII	6:00	220	05	180	32	23.34	23.03	15.91	14.77	13.36	11.83	12.66	15.94	16.84	17.04	6.40	7.10	11.20	12.10	12.50	4.98	3.60	0.00	0.00	0.00
	12:00	220	05	204	30	23.10	22.95	22.88	13.74	13.38	12.12	12.30	12.67	17.33	17.50	6.70	6.85	7.25	12.68	12.87	5.71	4.77	3.46	0.00	0.00
	15:00	220	06	275	24	23.41	23.24	19.30	13.32	13.21	12.08	12.15	13.38	17.41	17.53	6.58	6.70	8.56	12.82	12.92	6.17	5.97	2.66	0.00	0.00
18. VIII	9:00	300	14	196	36	22.00	22.03	16.58	14.90	14.91	12.73	12.77	15.36	17.13	17.17	7.42	7.46	10.64	12.30	12.33	5.19	5.12	1.44	0.00	0.00
	12:00	300	14	175	39	22.16	22.06	15.80	14.88	–	12.74	12.74	15.80	17.16	–	7.40	7.42	11.13	12.32	–	5.00	5.00	0.85	0.00	–
	15:00	300	12	200	36	22.01	21.69	14.99	14.84	–	12.68	13.01	16.73	17.21	–	7.34	7.71	11.98	12.38	–	5.72	4.89	0.12	0.00	–
	18:00	315	12	191	24	21.92	21.93	19.00	15.15	–	12.62	12.65	14.70	17.15	–	7.37	7.39	9.62	12.27	–	6.01	5.85	1.95	0.00	–
	20:00	300	10	260	40	21.81	21.81	21.82	17.68	14.88	12.63	12.63	12.63	15.90	17.18	7.40	7.40	7.40	10.83	12.34	5.90	5.90	5.93	1.04	0.00
	22:00	330	11	204	36	21.64	21.62	21.50	19.48	15.02	12.47	12.45	12.70	15.33	17.13	7.33	7.31	7.53	10.00	12.28	5.73	5.71	5.32	0.95	0.00

(continued)

Table 4.1 (continued)

Date	Time	Wind		Current[a]		T (°C)					S (‰)					σ_r					O_2 (mL/L)				
		Direction (°)	Velocity (m/s)	Direction (°)	Velocity (cm/s)	4	5	6	7	8	4	5	6	7	8	4	5	6	7	8	4	5	6	7	8
19.VIII	0:00	330	13	198	26	21.40	21.45	20.10	16.26	14.92	12.37	12.39	14.18	16.79	17.19	7.30	7.30	8.98	11.77	12.34	5.05	5.58	2.66	0.00	0.00
	2:00	320	14	258	32	21.22	21.24	17.34	15.06	14.79	12.26	12.32	14.74	17.09	17.21	7.27	7.32	10.02	12.23	12.39	5.21	5.18	2.02	0.00	0.00
	6:00	340	12	360	38	21.00	19.39	14.93	14.70	14.66	12.39	14.35	16.97	17.20	17.07	7.41	9.27	12.18	12.40	12.30	4.93	2.47	0.00	0.00	0.15
	8:00	340	15	10	27	20.79	18.12	14.66	14.54	14.41	12.35	15.86	17.13	17.26	17.29	7.43	10.72	12.34	12.48	12.52	4.83	1.79	0.00	0.00	0.00
	10:00	0	12	340	38	20.62	17.30	14.06	13.98	–	12.42	16.47	17.38	17.41	–	7.53	11.34	12.64	12.68	–	4.98	0.56	0.00	0.00	–
	12:00	20	11	30	24	20.54	15.26	13.82	13.76	–	12.54	17.01	17.46	17.47	–	7.63	12.14	12.58	12.59	–	4.80	0.24	0.00	0.00	–
	14:00	20	10	26	24	19.52	14.68	13.67	13.62	–	13.71	17.15	17.49	17.54	–	8.75	12.35	12.81	12.86	–	3.76	0.19	0.00	0.00	–
12.IX	13:00	290	06	290	13	19.95	19.81	15.04	13.70	13.68	13.69	13.92	16.32	17.44	17.52	8.64	8.85	11.68	12.76	12.83	6.65	6.49	0.00	0.00	0.00
	16:00	260	10	–		19.94	19.53	15.93	14.15	13.77	13.91	14.12	15.09	16.86	17.42	8.80	9.03	10.56	12.23	12.72	6.65	5.78	2.16	0.00	0.00
	18:00	280	10	–		19.90	19.65	19.04	16.97	14.04	13.86	13.99	14.29	15.38	17.37	8.76	8.94	9.30	10.59	12.65	6.23	6.22	4.82	1.15	0.00
	20:00	280	10	–		19.90	18.85	18.75	17.46	14.89	13.70	13.74	13.80	14.88	16.35	8.63	8.92	9.00	10.10	11.72	6.65	6.54	6.50	2.94	0.00
	22:00	280	12	–		19.83	19.90	19.83	19.86	15.50	13.70	13.70	13.77	13.80	15.68	8.68	8.67	8.72	8.75	11.10	6.32	6.56	6.37	6.49	1.20
13.IX	0:00	280	14	–		19.71	19.76	19.74	19.79	15.49	13.77	13.78	13.81	13.84	16.27	8.75	8.75	8.78	8.79	11.53	6.43	6.43	6.37	6.52	0.00
	6:00	300	12	–		19.39	19.34	19.43	19.35	15.28	13.74	13.71	13.75	13.81	16.60	8.80	8.80	8.80	8.88	11.83	5.78	5.86	5.81	4.39	0.00
	9:00	300	12	–		19.14	19.05	19.12	18.75	16.58	13.72	13.72	13.74	14.14	16.27	8.85	8.88	8.87	9.25	11.32	5.95	5.86	5.81	4.39	0.00
	12:00	295	10	–		19.17	19.15	19.13	19.02	17.15	13.88	13.80	14.06	14.26	15.67	8.99	8.91	9.11	9.29	10.77	5.56	6.01	5.78	4.71	0.84
	15:00	290	10	–		19.37	19.36	19.35	19.18	18.00	13.82	13.86	13.91	14.40	14.86	8.88	8.91	8.95	9.36	9.98	6.11	6.01	6.07	4.29	2.45
	17:00	260	07	–		19.44	19.45	19.46	19.40	18.75	13.67	13.83	13.72	13.80	13.97	8.74	8.88	8.78	8.85	9.12	6.13	6.29	6.29	5.91	6.30
	20:00	220	10	–		19.29	19.36	19.37	19.10	18.77	13.64	13.83	13.78	14.02	14.30	8.75	8.88	8.83	9.08	9.37	6.22	6.01	6.08	5.70	4.54
14.IX	9:00	260	09	300	20	18.69	18.69	18.8G	19.12	19.13	12.83	12.86	13.91	14.11	14.22	8.27	8.29	9.06	9.15	9.23	5.42	5.75	5.50	5.69	5.33

[a] The upper 5 m layer

light air, was disturbed again by stormy wind continued this time for about 1 day. Aeration of the deep layer proceeding during 15 h from the moment of the storm beginning, was also suppressed by powerful advection of waters in the bottom layer from the open shelf (Table 4.1). As the result, the upper boundary border of water hypoxia and hydrogen sulfide zone after that storm rose too. The oxygen content at depth of 6 m by the time of its termination decreased from 5.12 to 0.19 mL/L (Table 4.1, time 14:00 on August 19).

After the described August storms, the upper boundary of water hypoxia rose synchronously with the layer of the maximum density gradient (see Fig. 4.13 top A), and an oxygen deficit did not extend above the levels of its occurrence.

3. Quite different consequences of stormy wind were observed at the station on September 12–13. By that date, the hydrological situation here changed significantly. As a result of autumn cooling and general intensification of wind activity,

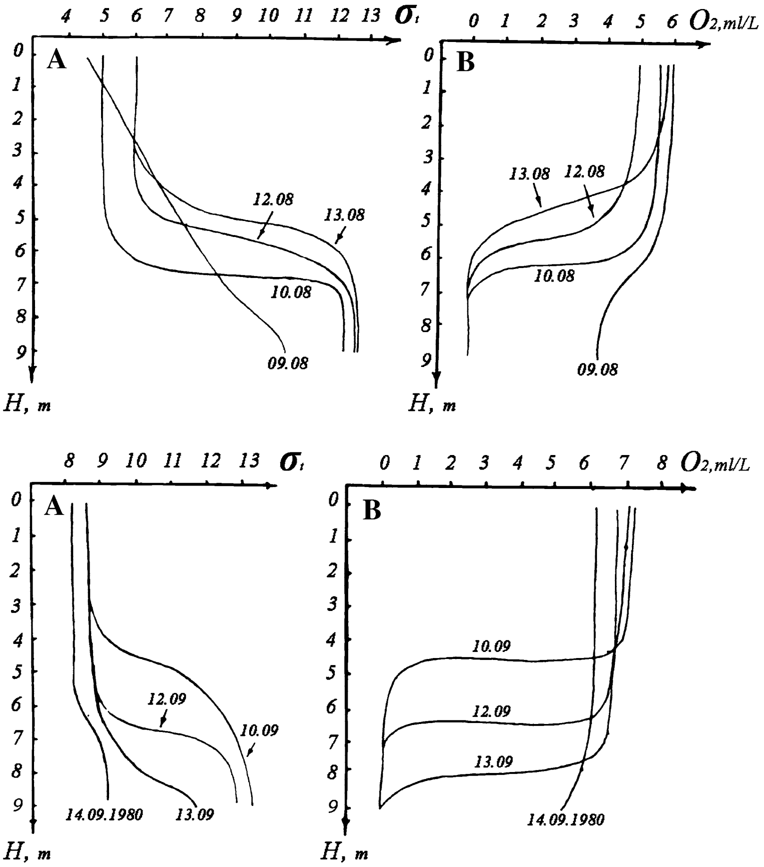


Fig. 4.13 Dynamics of vertical distribution of conventional density (**A**) and dissolved oxygen concentrations (**B**) under the suppressed (*top*) and favorable (*bottom*) vertical exchange at multiday station in the Tendra Bay during the storms, 1980 (Fashchuk et al. 1986)

the initiate mixing of shelf waters resulted in weakening of vertical gradients of temperature, salinity and conventional density of waters to 4.77°C, 2.20‰ and 2.83 of conventional density units per meter, respectively. Water stratification, thus, still persisted but was insufficient for suppression of vertical oxygen exchange (in this case, the Ri number was less than 10).

As late as 4 h after the storm beginning (16:00–20:00 on September 12) the oxygen content at depth of 7 m increased from 2.16 to 6.50 mL/L, and at depth of 8 m, from 0 to 2.94 mL/L. By 12:00 on September 13 (in 20 h) the aeration reached the near-bottom depth of 9 m, and the oxygen content here increased during this time from 0 to 0.84 mL/L; hydrogen sulfide (organoleptically) disappeared; and in another 5 h, a complete mixing of waters down to the bottom occurred (see Table 4.1; Fig. 4.13 bottom A, B).

After the correlation analysis of oceanographic time series obtained during the observations at the station, with the meteorological data for the same dates from the Ochakov hydrometeorological station, it was established (Fashchuk 1995) that:

- in summer, under conditions of the suppressed vertical oxygen exchange in the coastal areas of the northwestern Black Sea, with the maintenance of stormy (10–15 m/s) wind of northern quarter of more than 1 day, as late as 3–6 h after the beginning of its action, the oxygen regime at depths of 5–6 m is deteriorated due to advection of deep deoxygenated waters from the open shelf areas (increase in a thickness of the near-bottom anaerobic water layer), suppressing the process of wave mixing;
- at short strengthening of winds of the northern quarter, the similar deterioration of oxygen regime at depths of mussel collector placement occurs in 2–3 days after storm;
- mixing of water column on the shoal under the influence of wind waves occurs only in autumn after its cooling resulting in a decrease in stability and improvement of conditions of vertical oxygen exchange.

4.7.2 Influence of Synoptic Situations on Spatial Distribution and Dynamics of Anaerobic Zone in the Areas of Artificial Mussel Cultivation

Results of the experiments described in Sect. 4.1.2 allowed to identify the specific hydrometeorological conditions favoring the outcrop of anaerobic zone in locations of coastal aquaculture farms and to develop the practical recommendations on rational placing of mussel plantations in the Tendra Bay zone. The main results are the following:

- the first signs of water hypoxia in 1990 were registered on May 20–26 in the Danube area. By the end of June, the oxygen deficit in the near-bottom layer has already been observed on the whole coastal aquatory of the Danube-Dniester interstream; by July 25–30 the phenomenon spread to the coasts of Odessa, Ochakov, Dnieper offing, and in the Tendra Bay; in the late August—early September, it occupied more than 40% of the open shelf area. Hydrogen sulfide in the near-bottom layer was detected, beginning from the second half of July, in the near-mouth zone of the Dniester (0.2–0.5 mL/L; see Fig. 1.6);

- in the near-mouth area of the Dnieper and in the Tendra Bay hypoxia began to develop in May–June (Fig. 4.14a, b);
- short strengthening of wind of northern quarter up to stormy were noted on July 19–31, whereupon the presence of hydrogen sulfide of possible advective origin was noted organoleptically in the near-bottom layer at depths of 10–12 m along the coast of Ochakov and in the mouth of the Tendra Bay (Fig. 4.14c);
- after the storm under north wind on August 3–4, the aerobic zone, with the hydrogen sulfide content at the level of organoleptic determination (0.01 mL/L), on the Dnieper offing disappeared, while seawards of this area it continued to exist because the mixing effect was apparent only in the coastal zone (Fig. 4.14d);
- in late August—early September, the hydrogen sulfide concentrations in the near-bottom layer of the area under investigation reached 1.5–2.1 mL/L. With that, despite the north storms continued for 6–9 h (August 11, 19, 22, and 27), the anaerobic zone remained for almost a month, from August 15 to September 10 (Fig. 4.14e–i);
- in the beginning of autumn, with weakening of water stratification and intensification of mixing, the storms under north wind on September 13–14, as at the daily station in 1980, caused the aeration of the near-bottom layer of the Tendra Bay and disappearance of hydrogen sulfide here (Fig. 4.14k). The almost complete restoration of oxygen regime in the near-bottom layer of the area under investigation occurred after the storms on October 2–3 and 9–10.

At the individual site stations in the Tendra Bay (see Fig. 4.14), during the experiment conducted in spring-autumn, 1990 (11 repeated oceanographic surveys), the upper boundary of water hypoxia changed in different ways (Fig. 4.15):

- in the central part of the bay (sta. 44, 45, Fig. 4.2b) and off the northernmost tip the Tendra Spit (sta. 43, Fig. 4.2b), at the sea depths of 15, 12, and 13 m, the maximal vertical development of hydrogen sulfide zone reached 6, 5, and 7 m, respectively, and the water hypoxia layer in these cases made up 8, 6, and 10 m;
- at more shallow stations (5–8 m) located in the coastal zone of the bay, along the Kinburn and Tendra Spits (see Fig. 4.2b), and in the area of artificial mussel plantations (sta. 50, Fig. 4.2b), at the sea depth of 9 m the thickness of near-bottom hypoxia layer fluctuated within 2–5 m, and that of hydrogen sulfide zone, within 1–3 m (see Fig. 4.15);

In late summer, in the coastal zone, in the area of Ochakov (sta. 55, Fig. 4.2b), the effect of offshore north storms is seen in displacement of waters with hypoxia from depths of 10–15 m onto the shoal (5–6 m) and their outcrop here and at the beaches, together with cold (<16°C) and saline (>16.5‰) water (Fig. 4.16b, f, d).

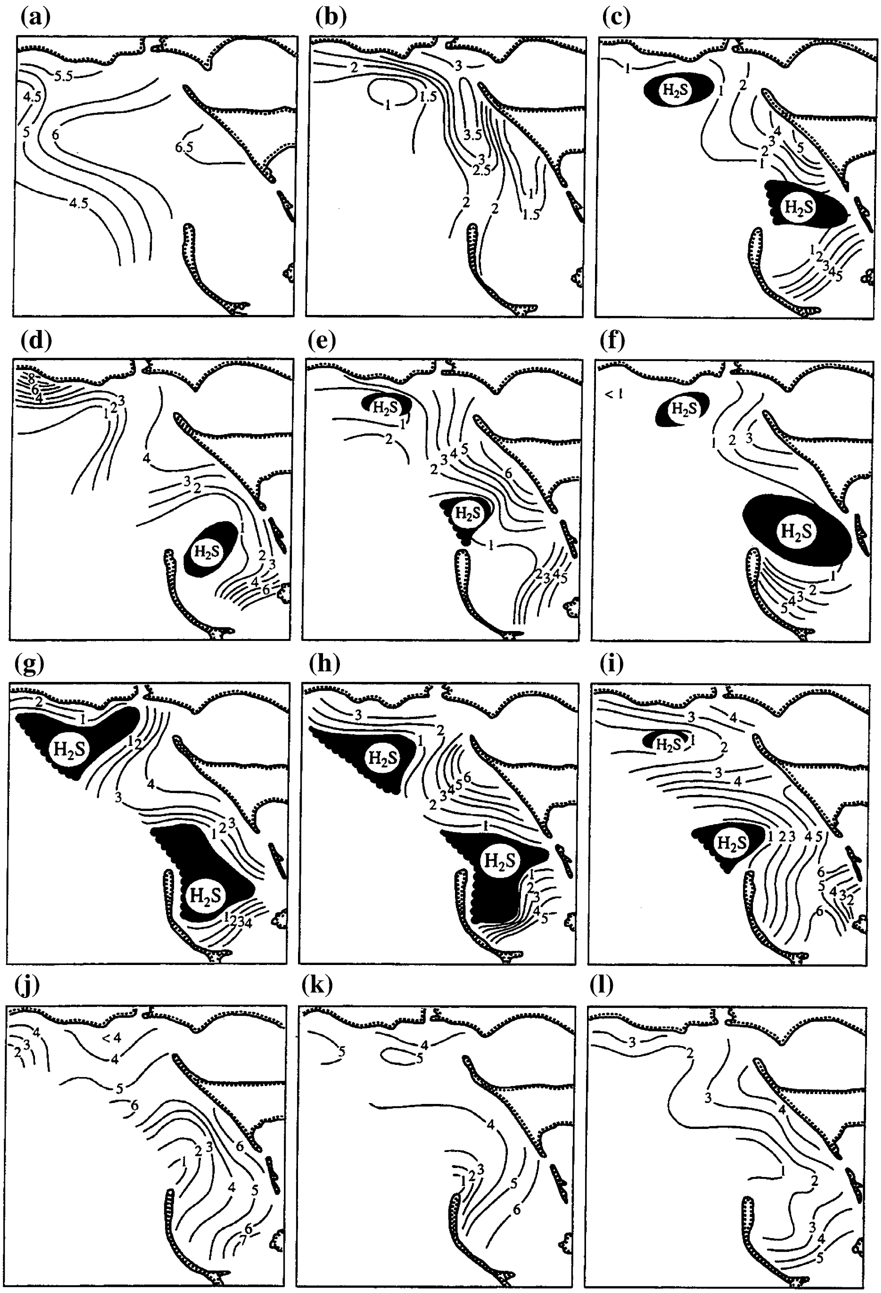
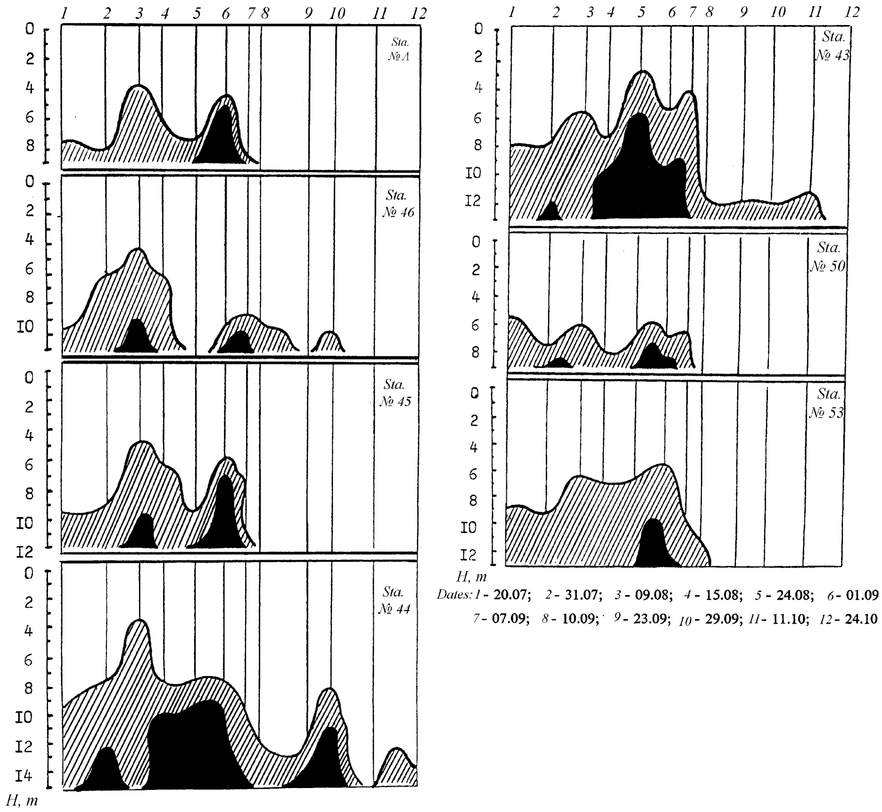


Fig. 4.14 Distribution of oxygen (isolines, mL/L) and position of hydrogen sulfide zone (*shaded areas*) in the near-bottom layer on the Dnieper offing and in the Tendra Bay, 1990 (Fashchuk 1995). **a** May 26, **b** July 20, **c** July 31, **d** August 9, **e** August 15, **f** August 24, **g** September 01, **h** September 7, **i** September 10, **k** September 23, **l** October 11



Dates: 1 - 20.07; 2 - 31.07; 3 - 09.08; 4 - 15.08; 5 - 24.08; 6 - 01.09
7 - 07.09; 8 - 10.09; 9 - 23.09; 10 - 29.09; 11 - 11.10; 12 - 24.10

Fig. 4.15 Dynamics of the upper boundary of water hypoxia (*hatching*) and hydrogen sulfide zone (*dashed areas*) at several stations of the site in the Tendra Bay (see station numbers in Fig. 4.2b) by results of the repeated surveys in spring-autumn, 1990 (Fashchuk 1995; see Fig. 4.2b for explanatory notes)

In the Tendra Bay at this time, the H_2S-containing waters from the open shelf penetrate into the center of the bay where their upper boundary rises (depth of 10–12 m) to depths of (Fig. 4.16f). In the period of maximal development of anaerobic conditions, when the hydrogen sulfide concentration in shelf waters exceed 1.5 mL/L (as in the open Black Sea at depth of 200 m), its reserve in the near-bottom layer is sufficient for these waters to reach the surface in the coastal zone under the influence of the offshore-inshore circulation and to stand up to the mixing process in the more outshore shelf areas, despite the intensive oxidation of hydrogen sulfide in this case.

For the 1971–1989 period at the hydrometeorological station of Ochakov, 25 cases of storms were noted, on the average, in June–September under winds of northern quarter (11 cases of northeast and 9 of northwest direction). Most often north stormy winds are observed here in August (9 cases, on the average, with a maximum up to 20 cases). Thus, August is most dangerous month for artificial

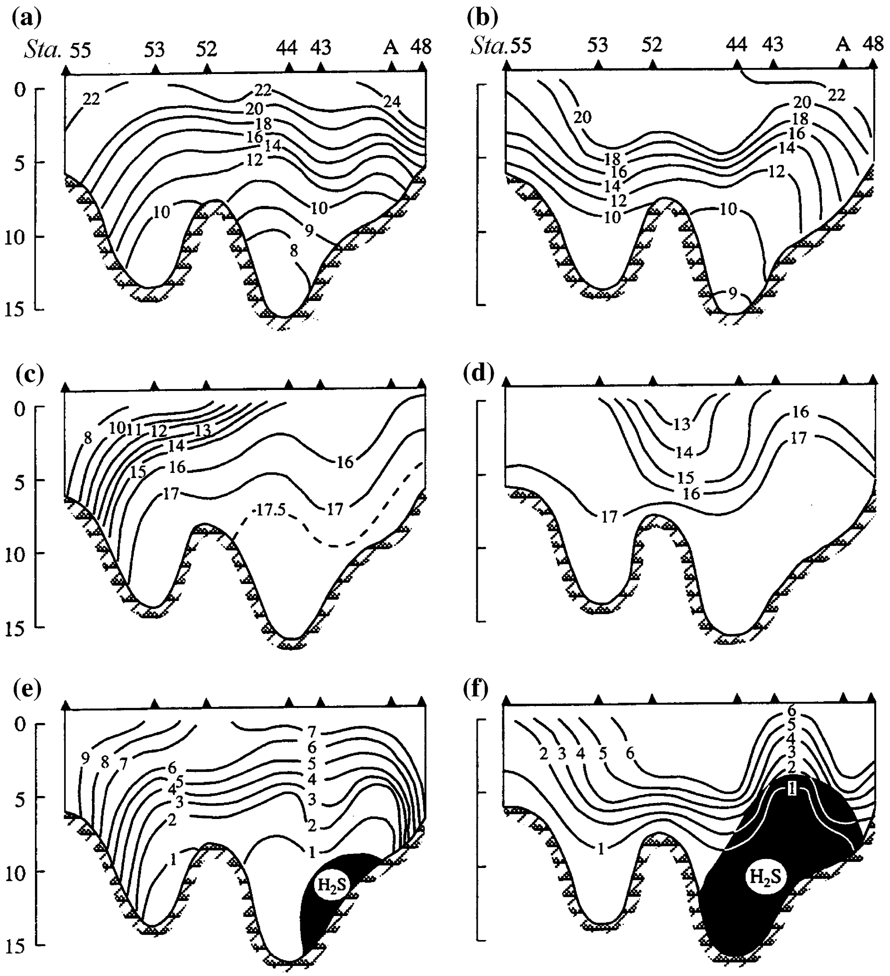


Fig. 4.16 Distribution of temperature, °C (**a**, **b**); salinity, ‰ (**c**, **d**); dissolved oxygen, mL/L (**e**, **f**) at meridional section from the coast (sta. 55) to the Tendra Spit (sta. 48) before (**a**, **c**, **e**) and after (**b**, **d**, **f**) stormy offshore north wind in August, 1990 (Fashchuk 1995) (see station numbers in Fig. 4.2b)

cultivation of mussels in the coastal zone from Odessa to Ochakov and in the Tendra Bay because of the rather high probability of lifting of H_2S-containing waters, up to their outcrop (Photo 4.20).

However, when allocating mussel plantations in the area under investigation at depths down to 5–6 m, or in the surface layer of the open Tendra Bay on collectors with length up to 3 m, the development of ecological crises, even under the extreme conditions, such as north (offshore) storms, will not affect the process of artificial cultivation of mollusks.

Photo 4.20 Plantations for artificial cultivation of mussels in all regions of the World ocean look approximately identical: collectors (inset vertically dangling ropes (Photos 4.18, 4.19), with length up to 10 m and foam plates covered with capron net, on which larvae of mollusks settle, attach and develop to market condition) are strengthened to the thick rope (Photo by M. Pereladov) tense in the sea (mainline), which ends are fixed on anchored buoys, with spacing of 1–2 m

4.7.3 Real-Time Search of Commercial Sprat Concentration on the Black Sea NW Shelf

The sprat fishery in the northwestern Black Sea during the spring-summer period started to develop intensively from the early 1970s. At this time, formation of fish concentrations in the area is encouraged by the near-bottom water temperature of 6–9°C; existence of pronounced vertical density gradient; and the high concentrations of fodder zooplankton. Traditionally, search of commercial sprat concentrations was conducted according to these indications and was rather effective in the real-time practice. (Fashchuk 1998).

From the late 1970s, the accuracy of fishery forecasts in the northwestern Black Sea decreased sharply. Fish ceased to form commercial concentrations in the areas with the above-mentioned favorable conditions, stood in sparse state, was very mobile and detached from the bottom. Sometimes, mass “panic” migrations of fish to the coast, in the zone of beaches, were observed (Photos 4.21, 4.22).

In spite of the fact that sprat is a pelagic species (inhabiting the water column), during the feeding period of its life cycle it migrates into the near-bottom water layer of the NW shelf and onto the continental slope (70–100 m) in the same area and in the western sea. To identify the causes of the changes in behavior of sprat, during the spring-summer periods, 1979–1985 we carried out a complex of the targeted natural experiments (more than 20 expeditions) on the ecological site in the northwestern sea and open areas of its western part (see Fig. 4.2a), included parallel oceanographic, hydrobiological, trawling surveys and multiday stations. As a result of these works, the new features of environmental conditions were revealed. Their comparison with the traditional ideas enabled to clear the reason of decrease in accuracy of real-time fishery forecasts and to develop practical recommendations in this context:

Photo 4.21 Sprat shoals feeding in the near-bottom layer of the shelf, overtaken by anaerobic zone driven by offshore wind, migrate sweepingly in front of it to the coast, and some individuals even jump out of water, escaping from asphyxia (Photo by O. Kudinsky)

Photo 4.22 With approaching the hydrogen sulfide zone to the coast, less mobile bottom inhabitants of the sea are a sitting duck for sea gulls (Photo by O. Kudinsky)

1. During the summer period the northwestern Black Sea areas with temperature regime in the near-bottom layer, favorable for sprat concentrations, coincided with the zones of near-bottom hypoxia and anaerobic conditions (see Fig. 4.4).
2. The northwestern Black Sea areas with the well-developed, up to 0.2 of conventional density units and more per meter, layer of density gradient (other favorable condition for sprat concentrations) are also occupied by near-bottom hypoxia and anaerobic zones because it is the conditions that determine development of these phenomena in summer.
3. The food factor, under the conditions of hypoxia development, loses its ecological importance for sprat. Even at concentration of food zooplankton above the pycnocline during day and nighttime, equal to 1,150 and 431, and in the near-bottom layer—to 369 and 851 mg/m^3, respectively (10 times higher than values registered at the high catches of sprat in the 1950s–1960s), in case of the oxygen content in the near-bottom layer less than 1 mL/L, fish do not form commercial concentrations in the shallow (25–30 m) near-mouth areas.

4. On the edge of the NW shelf (70–100 m), under the influence of periodically passing anticyclonic eddies, advection of deep, depleted with oxygen, waters into the shelf zone (see Fig. 3.14) is noted during the fishing period. In spite of the fact that their temperature (7–8°C) falls into the favorable for sprat range, the low oxygen content (0.4–0.6 mL/L) does not allow fish to concentrate also at these depths.

Thus, today the traditional indicators for search of the areas of commercial sprat concentrations have been replaced by new factor, an oxygen regime of near-bottom waters. The sites located between isooxygenes of 3 mL/L, confining from the north the seasonal hypoxia zone (down to 30 m) on the shoal and zone of advection of deep, depleted with oxygen, waters from the open sea onto the shelf (down to 70 m) from the south, are the most probable areas of fish concentration on the NW shelf during the summer period, providing the presence of appropriate temperature conditions and food base in the above “hydrochemical corridor”.

4.8 Conclusion

The geographic and ecological approach to identification of the causes of intensification of seasonal ecological crises, suffocation events, on the northwestern shelf of the Black Sea has allowed:

- to develop a working hypothesis of study, based on external indicators of the catastrophic phenomenon realization, such as mass kill of bottom fishes, mollusks and seaweed;
- to estimate the priority natural and anthropogenic mechanisms, responsible, according to the hypothesis, for deterioration of oxygen regime in the near-bottom water layer of the shelf;
- to plan and conduct a complex of the targeted field experiments which results enabled to estimate the spatial and temporal (interannual and synoptic) variability of the hypoxia and anaerobic zones, to establish timeframe of their appearance, depending on the external environmental conditions, and the specific factors determining their formation and dynamics;
- to assess the possible climatic and anthropogenic prime causes of change in environmental conditions on the NW shelf during the spring-autumn period that determined finally the intensification of ecological crises;
- to obtain the reliable original data for realization of the model of chemical kinetics of anaerobic zone and, after its realization, to make prognostic estimates of possible time of its existence and character of transformation, depending on hydrometeorological conditions;
- to develop practical recommendations on rational ecosystem exploitation, including artificial cultivation of mollusks and sprat fishery, in the investigated region under conditions of developing ecological crises.

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Chapter 5
Gas Production on the Northwestern Shelf of the Black Sea: Scales, Geographic and Ecological Conditions, Consequences and Their Forecast

The northwestern shelf (NWSH) is not only the most productive region of the Black Sea. At the end of the XX century this aquatory became an arena of intensive economic activities. Among a variety of its forms (see Fig. 1.13) the development of marine gas fields by Ukraine is ecologically the most actual.

5.1 Oil-and-Gas Content of the Azov-Black Sea Basin

Such are the features of tectonics and history of development of the Black Sea basin (The Earth crust … 1975) that in meridional direction it is crossed by 14 large deep geological faults (Fig. 5.1) separating structural elements of the Black Sea Coast: the East European craton—Carpathians—Carpathian basin; the East European craton—Scythian plate—Mountain Crimea; the Misean plate, the Balkans—Southern Carpathians; the Crimea—Caucasus and the Black Sea basin.

In Chap. 3 of the monograph, when investigating the possible reasons of the sea fires observed in 1927 during the Crimean earthquake near Sevastopol at Cape Lukull, it was noticed that "the sea burnt" over one of such faults, the Krivorozhsk–Yevpatoria fault (section E, Fig. 5.1). In the zone of this fault, as well as on three others faults crossing NWSH in meridional direction (sections B, C, D, Fig. 5.1), in winter and summer, 1989–1990 researchers from the Institute of Biology of the Southern Seas (InBYUM) of the Academy of Sciences of Ukraine discovered the underwater gas emissions consisting by 80% from methane (see Fig. 3.27).

As a result of the same field works conducted by InBYUM from a sea bed vehicle along the Caucasian coast from Sukhumi to Batumi at depths from 25 to 850 m, 17 sources of gas emission were investigated. The most powerful source was located at depth of 540 m and had more than 400 m in its diameter. In the area

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Environmental Science and Engineering, DOI: 10.1007/978-3-642-17444-5_5,

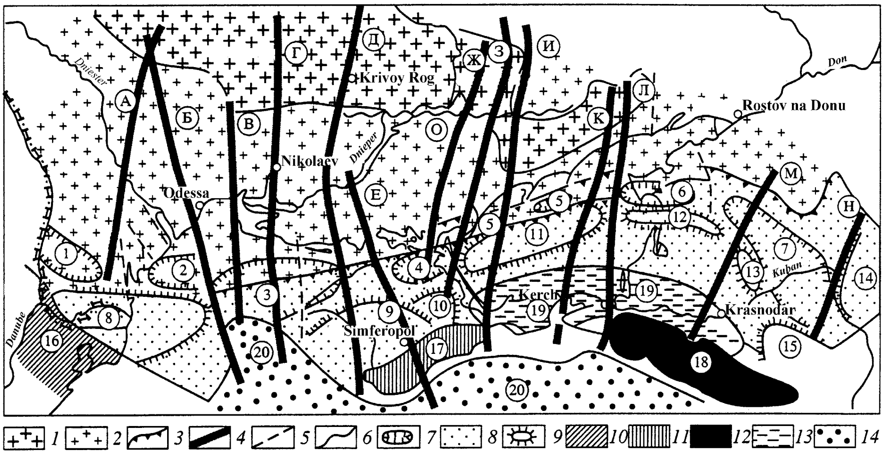


Fig. 5.1 The scheme of ancient faults of the North Black Sea Coast (The Earth crust … 1975). *Explanatory notes*:*1* exposed part of the Ukrainian Shield, *2* shield slope, *3* border of the East European craton, *4* ancient deep submeridional faults, *5* large faults, *6* ancient sublatitudinal deep faults, *7* contours of grabens of the Black Sea–Kuban basin, *8* Scythian plate, *9* contours of uplifts of the Scythian plate, *10* outcrops of Baikal–Hercynian–Cimmerian orogenic structures, *11* outcrops of Cimmerian orogenic structure, *12* outcrops of Jurassic–Paleogene orogenic structures, *13* Alpine fore-basin, *14* Alpine intra-synclinal superimposed depression. *Letters on the scheme—ancient deep faults*: *A* Frunzensk–Artsiz, *B* Odessa, *C* Ochakov (Ryasnopolsk), *D* Kirovohrad–Mikolaiv, *E* Krivoy Rog–Yevpatoria, *F* Salhir–Oktyabrsky, *G* Konsk–Belozersk, *H* Orikhiv–Pavlohrad, *I* Korsaksko–Feodosiya, *J* Mariupol–Kerch, *K* Kalmius–Dzhginsky, *L* Afipsky–Ekaterininsky, *M* Armavir–Takhtinsky, *N* Zlatopol–Konkinsky. *Tectonic structures* (figures on the scheme): *Black Sea–Kuban basin* (1–7): *1* Moldavian trough, *2* Krylov trough, *3* Odessa trough, *4* Sivash trough, *5* North Azov troughs, *6* Yeysk (Kopansky) trough, *7* East Kuban trough. *Scythian plate* (8–14): *8* Kiliya uplift, *9* Simferopol–Yevpatoria uplift, *10* Novotsaritsynsky nose, *11* Azov arch, *12* Kaniv uplift, *13* Berezan uplift, *14* Stavropol anticlinal fold. *15* Adygeya nose, *16* folded structure of Dobruja, *17* Mountain Crimea, *18* Greater Caucasus, *19* Indol–Kuban trough, *20* Black Sea basin

of Karadag (Feodosiya) and the Kerch Strait the similar phenomenon was fixed in 15 sites at depths from 87 to 400 m, and along the coast of Romania and Bulgaria—in 38 sites located in a depth range of 99–590 m (Polikarpov et al. 1990).

By the beginning of the XXI century about 120 promising oil-and-gas bearing structures were discovered on the aquatory of the Black and Azov Seas by method of seismic exploration. *The volume of potential retrievable hydrocarbon resources* in the Sea of Azov is estimated within 200–670 million t of oil equivalent (o.e.), and that in the Black Sea—in 560–2330 million t. *The projected reserves of hydrocarbons* on the shelves of the Black and Azov Seas are estimated in 1,532 million t of o.e. From them, 1,207 million t of o.e. (79%) are contained in the fields of the Black Sea, and 325 million t of o.e. (21%)—in the Sea of Azov. From the total hydrocarbon reserves of the Black Sea projected in terms of oil equivalent, 257 million t are deposited on the shelf adjacent to Kerch, 387 million t—on the continental slope and in the deepwater basin, 654 million t—on the northwestern shelf. In actual figures, in the Sea of Azov it is possible to extract 30, in the Kerch–Taman area—162, and on the northwestern shelf of the Black Sea—more than 100 billion m^3 of gas. For comparison, the potential hydrocarbon resources on the shelves of all marginal seas of Russia are estimated in 90–100 billion t of oil equivalent, from which gas constitutes 80%. The potential reserves of only the Barents–Kara and South Kara basins make 50–60 billion t. The gas reserves of the world's largest Shtokman field (Barents sea) are estimated in 3.2 trillion m^3 that is commensurable with gas fields in Yamal; in the Pechora Sea, only from one field of Prirazlomnoe the retrievable oil reserves (30% of estimated reserves) make 74 million t, and those of gas—8.6 billion m^3; the projected retrievable reserves of oil on the shelf of Sakhalin Island are more than 1.5 billion t (Patin 2001), and whole Western Siberia contains 9.1 billion t of the proved oil reserves (Osadchyi 2006).

From the results of comparison it is obvious that hydrocarbon resources of the Azov-Black Sea basin are much more modest than those on the shelves of marginal seas of Russia. Nevertheless, this potential appears rather considerable for Ukraine. Annually, this country consumes from 66 to 76 billion m^3 of natural gas, from which only 22 billion t are the own production in the Eastern, Western and Southern oil-and-gas bearing regions of the country. The last region includes aquatories of the Ukrainian sector of the Black and Azov seas, and adjacent land areas of the plain Crimea, Northern Black Sea Coast and Azov Coast. With that, about 85% of potential hydrocarbon resources of the Southern region are deposited under marine aquatories.

5.1.1 The Sea of Azov

The study of geological structure of the Azov Sea bed and shelf of the Black Sea by seismic methods started in the 1960s. There are two oil-and-gas bearing regions in the Sea of Azov: the Vysokovskaya area in territorial waters of Ukraine (southwestern sea) and the Paleozoic area in territorial waters of Russia (central sea).

The discovery of Strelkovoye gas field (Vysokovskaya area) on the land–sea border in 1963 became the first confirmation of oil-and-gas bearing capacity of the Azov Sea aquatory. The exploratory drilling in the Sea of Azov has begun only in June, 1975. As a result, within the Ukrainian sector of the sea another six gas and gas condensate were discovered: Strelkovoye (1976), Morskoye, North Kerch, North Kazantyp (1998), East Kazantyp (1999), and North Bulganak (2000). Three of them, Strelkovoye, East Kazantyp, and North Bulganak, were placed on industrial production in 1981, 2002 and 2004, respectively. Gas reserves in the Strelkovoye, East Kazantyp, and North Bulganak fields are estimated in some

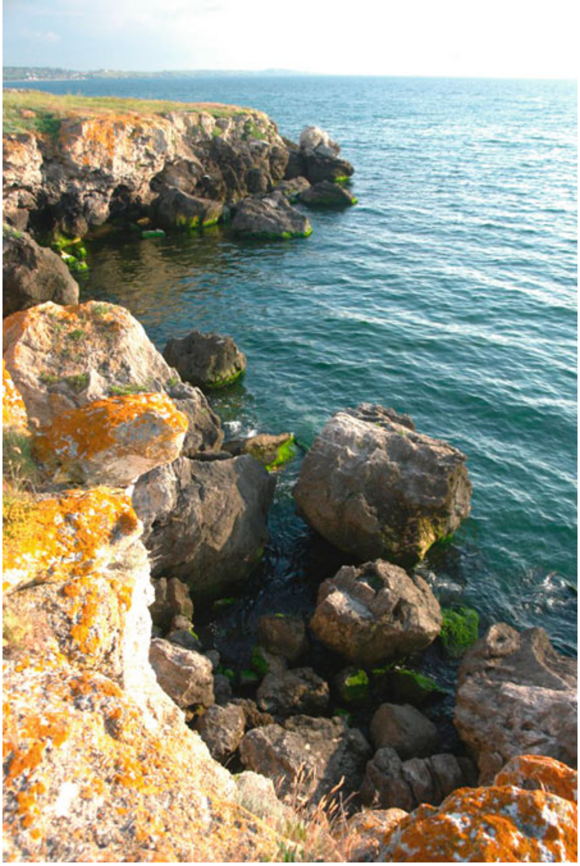


Photo 5.1 Coasts of Cape Kazantyp in the Sea of Azov (photo by A. Kopeikin)

billion m^3 each. The North Kerch, North Kazantyp, and Morskoye fields are suspended now (Photo 5.1).

5.1.2 The Kerch–Taman Shelf and Coastal Zone

The total area of Kerch oil-and-gas bearing site is 13 thousand km^2. The sea depths here vary from 40 to 2000 m. In 2004, State JSC *Chernomorneftegaz* has begun, and in January, 2006 has finished the drilling of parametric well No. 403 on the Subbotino structure. Oil was found at depth of 4,300 m under the sea bed (sea depth is 40 m). The potential resources of this structure were estimated in 257 million t of oil equivalent. In 2007, the first exploratory well (3,200 m) was drilled and tested, which confirmed its commercial oil reserves in the volume of 100 million t. In 2008, the second exploratory well has been drilled there, and the production testing of two wells has started. For the moment, the wells of Subbotino oil site produce 406 million m^3 of associated gas (about one-third of the present production volume of *Chernomorneftegaz*). Until 2016, about 80 wells are planned to drill here, from which 40 wells will be placed on production (Maskalevich 2008).

The Pallas Uplift is also of a great interest in terms of oil-and-gas bearing capacity of the Kerch–Taman coastal zone. It is a component of the large North Black Sea Uplift, the northern sites of which are moved under the geological formations of the Kerch–Taman shelf.

In particular, such promising structures as the Tuapse Trough, Shatsky Arch, Andrusov Arch, Moryan and South Kerch structures, Teteev High, Sorokin Trough are distinguished on the Pallas Uplift. The sea depths here range from 500 to 2,000 m. In 2007, the three-dimensional seismic surveys were conducted on the Pallas Uplift, within aquatories of its northwestern and southeastern sites (150 km from Gelendzhik). It is expected that resources of the southeastern site make 50–100 million t of oil equivalent, those of the northwestern site—150–300 million t, and retrievable reserves of natural gas are estimated in 78 and 98 billion m^3, respectively.

About four-fifths of the Pallas Uplift area are located in the Russian territorial waters. In the absence of technical means for drilling at sea depth of more than 70 m, Ukraine plans to begin drilling of exploratory wells on the Pallas structures and in the Tuapse northwestern Black Sea area only in 2009, after acquisition of the corresponding equipment (Maksimov 2008).

In 2007, the total marine gas production by Ukraine made 1.26 billion m^3, and that of oil and gas condensate was 80 thousand tons. For comparison, to the south of the Snake Island the Romanian company *Petrom* develops the East and West Levada fields, extracting about 2 million t of oil from seven platforms annually. Oil in a year. After the beginning of commercial production of the Odessa and Bezymyannoye fields on the northwestern shelf of Black sea by Ukraine, planned for 2009 year, it is projected to increase the total marine gas production by 1 billion m^3, i.e. almost 2 times, and due to putting into production of new wells, by 2017 Ukraine intends to increase the annual gas production to 3 billion m^3 (2.5 times), and production of oil and gas condensate—to 1.8–3.5 million t (20–40 times) (www.NTWSru.ua).

5.1.3 The Northwestern Shelf of the Black Sea

From 133.7 thousand km^2 of the Black Sea northwestern shelf total area (see Photo 4.1), the oil-and-gas bearing region occupies about a half. The underwater sources of gas emission in the northwestern sea are located in the zones of four deep tectonic faults of the North Black Sea Coast: Odessa, Ochakov, Kirovohrad–Mikolaiv, and Krivorozhsk–Yevpatoria (see Fig. 5.1). The exploratory drilling on the northwestern shelf of the Black Sea began in September, 1971 on structure Golitsyno.

The commercial production of gas started here in 1983 on the stationary sea platforms (SSP) *Golitsyno*-4, 5 and *Shmidt*-6 (it was suspended in 1990), located in the western and central parts of the Karkinit Bay aquatory (Fashchuk et al. 2006a, c). In the mid-1980s the exploratory drilling was also conducted on wells *Golitsyno*-2, 18, and since 1990 *Chernomorneftegaz* has started their commercial development.

In April, 1989 the SSP *Karkinitskaya*-19 was set in the Karkinit Bay; the exploratory drilling began here in July and ended in August. In the 1990s, to the south of the SSP complex *Golitsyno*, at distance of 25 km from Cape Tarkhankut, the Arkhangelskoye (reserves of 15–18 billion m^3) and Shtormovoye (reserves of about 20 billion m^3) gas fields were discovered. The exploratory SSPs *Arkhangelskaya*-7 (1992), *Shtormovaya*-17 (1993) and projected *Shtilevaya*-1 were set on these fields. The total annual gas volume produced by Ukraine on the NWSH of the Black Sea in the early 1990s was about 500 million m^3.

In 1997, in the central part of the NWSH the Bezymyannoye gas field (reserves of 20–25 billion m^3) was discovered. In 2007, close to it, at distance of 50 km to the east from the Snake Island (Photo 5.2) and of 65–70 km from the already developed Golitsynsky and Shtormovoye fields, the Odessa field, with gas reserves of 22 billion m^3, was discovered.

The sea depth here is 43 m, and depth of hydrocarbon occurrence is 1620 m. As a whole, 13 fields and oil-and-gas bearing structures with small reserves of gas and gas condensate (10–50 billion m^3 each) were discovered in the Snake Island area (Grinevetsky et al. 2007).

Photo 5.2 The area of the Snake Island located in the Black Sea at distance of 37 km from the Kiliya armlet of the Danube delta, is only 1.5 km^2, height—40 m above sea level by [www.focus.ua]

5.2 Natural Factors of Dynamics and Transformation of Pollutants on the NW Shelf

To estimate the possible consequences of marine gas production for ecosystem of the northwestern shelf of the Black Sea and to forecast the state of environmental conditions and inhabiting hydrobionts, we developed its geographic and ecological information model which included physico-geographic features, natural processes affecting the dynamics, transformation and accumulation of polluting substances (PSs) in water and bottom sediments; the estimation of contribution of other anthropogenic sources to the total level of shelf pollution; the analysis of distributional features and structure of populations of commercial fishes and their food objects, biocenoses of commercial mollusks and seaweed (Egorov and Fashchuk 2003).

The geographical position of the Black Sea (46°33’–40°56’N, 27°27’–41°42’E) determines the essential differences of physiographic characteristics of its separate areas and aquatories. The northern part of the basin is located in the zone of moderate climate, while its southern part—in the zone of subtropical climatic belt. Moreover, the coast and sea bottom have a number of geomorphological features associated with its geological history (see Chap. 3). They determine the considerable spatial variability in character of natural and anthropogenic processes impact on marine environment of its various areas, and, consequently, and on the rate and character of oil product transformation in marine environment, time of self-cleaning of the sea from oil pollution.

5.2.1 Physico-geographic Features

The area of shallow coastal zone of the Black Sea (down to 200 m) is 124,840 km^2. From them, the northwestern shelf occupies 39%, i.e., about 48,334 km^2. The length of its coastline makes about 1,000 km, water volume in the depth range of 0–100 m reaches 854 km^3, mean depth is 17.3 m, and the maximal width reaches 200 km (Simonov and Altman 1991).

The northwestern shelf zone includes the southern edge of the East European Paleozoic craton and the Epipaleozoic Scythian Platform, has a weak inclination (5–8°) and flat abrasion-accumulative relief, in which the ancient valleys of the Dnieper, Dniester, and Danube Rivers are traced at distance to 100–120 km from the coast. The Budaksk, Dniester, West Tendra Highs, and the Odessa and Karkinit Depressions are located on the sea bed (Fig. 5.2).

The depths over highs reach 15–20 m (over the Dniester High—10 m), and in the centers of depressions—25–30 m (Fesyunov and Nazarenko 1991). The coasts are considerably dissected by shallow bays, such as the Zhebriyansky, Odessa, Yagorlytsky, Tendra, Dzharylgachsky, Karkinit Bays. Four largest Black Sea rivers, the Danube, Dnieper, Dniester, and Southern Bug, run into the area.

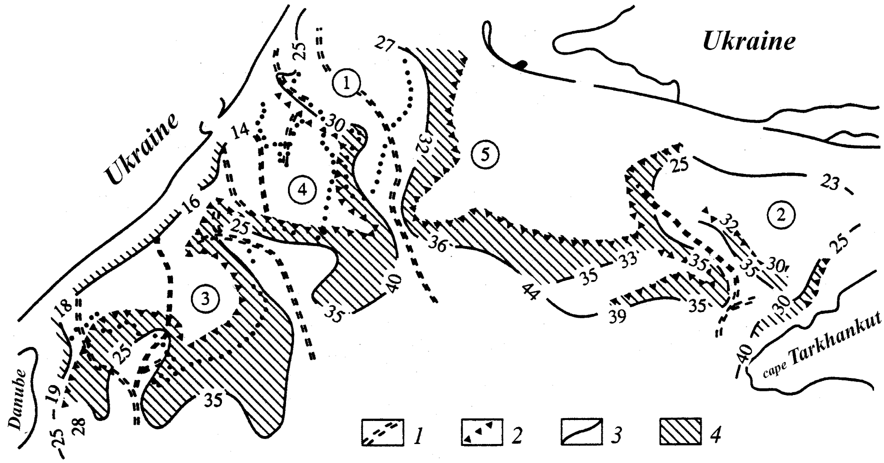


Fig. 5.2 The scheme of relief of the coastal northwestern shelf of the Black Sea (Fesyunov and Nazarenko 1991). *1* axes of relief depressions, *2* edge of slope of highs, *3* bottom of slope and its depth, m, *4* slopes. *Circles*: *1*, *2* Odessa and Karkinit Highs; *3*, *4*, *5* Budaksk, Dniester, and West Tendra depressions

Annually, it averages 260 km^3, or 80% of the total river discharge into the Black Sea. The total watershed area of these rivers is 1.45 million km^2. With that, the watershed areas of each river make 817, 505.8, 72, and 68 thousand km^2, respectively, or 44, 27, 5, and 5% of the watershed area of whole Black Sea, constituting 1,874,904 km^2 (see Fig. 1.19). The value of specific watershed, the ratio of its area to the area of marine aquatory receiving the river drainage, is about 29 that reflects a very high degree of dependence of the sea on the land (Zaitsev 1992).

The considered physico-geographic features of aquatory of the northwestern shelf of the Black Sea define a specific combination of natural factors determining the formation of marine environment conditions here (Photo 5.3).

The dominant influence of the long-term variations in atmospheric circulation and river runoff on changes in the oceanographic regime and hydrodynamic conditions, and on bioproductivity level is a characteristic feature of the Southern Seas of Russia during the last 50–60 years (Matishov et al. 2008).

5.2.2 Heat Balance and Waters Oceanographic Characteristics

In the annual course of solar radiation practically in all areas of the Black Sea its maximum is observed in June–July, and the minimum—in December. The flux of direct solar energy is substantially transformed by cloudiness. In the northern sea only 64%, and in its southern part—95% of its total amount reach the sea surface that makes 3,770 and 5,860 MJ/m^2, respectively. From them, only 65–80%

Photo 5.3 Waters of the Karkinit Bay wash limestone rocks of Cape Tarkhankut, the westernmost point of the Crimea (Photo by A. Kopeikin, V. Matskevich)

are absorbed and participate in formation of the thermal balance of the sea. The absorbed solar radiation reaches maximal values in June, when its receipt is large, and cloudiness is insignificant. Taking into account the heat losses due to evaporation, which maxima are noted in the northwestern and open northeastern sea, the thermal balance of the Black Sea in the mean annual plan is negative in the northern part and positive in the southern sea.

As a whole, the thermal regime of surface Black Sea waters is characterized by seasonal persistence of the temperature minimum in the northwestern Black Sea (Fig. 5.3). In winter, surface water temperature on the open shelf may drop to 2–4°C, and in the coastal areas and Karkinit Bay—to the ice point. The temperature minimum is reached in February.

The warming of surface layer begins in March, and by May the temperature maxima limited to the mouth areas, reach 15–16°C, and the minima corresponding to the areas less affected by river runoff (the Karkinit Bay), make 13–14°C. By the end of spring the surface layer warms up to 18.5–19.5°C, and in summer—up to 23–24°C, at a minimum of 21–22°C. The temperature maximum is reached in August.

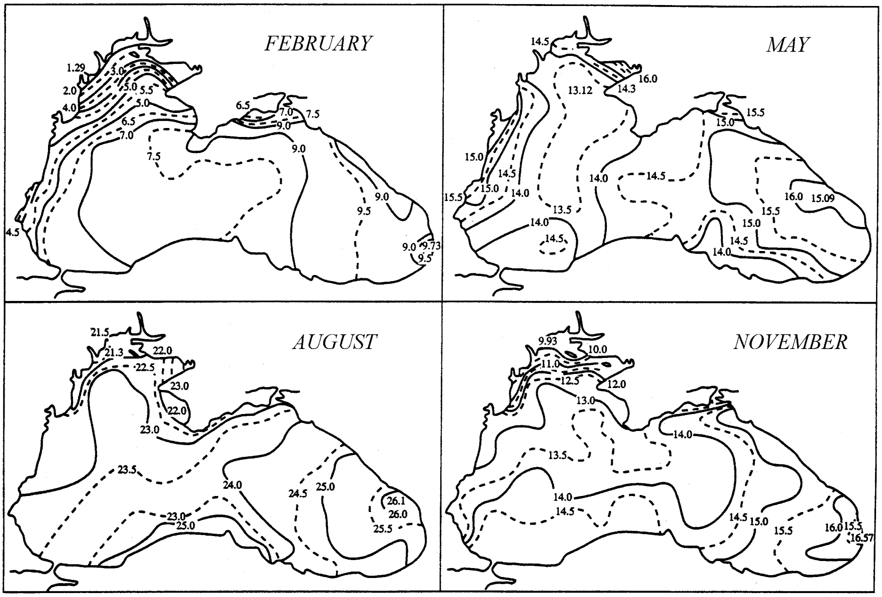


Fig. 5.3 Mean long-term temperature pattern (°C) on the Black Sea surface (Project "The Seas…" 1991)

Photo 5.4 Winter, 2005–2006 was one of the severest in the Azov–Black Sea basin for the last 50 years. The ice thickness in the Sea of Azov reached 0.5 m, and height of ice ridges—1.5–2.5 m (Photo by A. Kopeikin)

The autumn cooling begins in September, and by November almost the whole open shelf is occupied by water with temperature of 13–15°C. With that, the spatial range of its variations can reach 6.5°C (Photo 5.4).

The vertical distribution of water temperature on the northwestern shelf is characterized by presence of the seasonal thermocline (ST) and upper mixed layer (UML), which begin to form with spring warming (March). The maximal vertical temperature gradients in the ST-layer can reach 10–15°C/m, and the UML thickness in summer varies from 2–5 to 10–15 m in the coastal and its open part, respectively (Fashchuk 1995). The presence of such vertical structure may essentially change the character of redistribution and intensity of transformation of polluting substances on the shelf aquatory.

The estimation of mean annual values of oceanographic regime characteristics in the areas of setting of marine drilling platforms on the NWSH of the Black Sea was made with the use of the long-term (1955–1991) seasonal field investigations conducted by Southern Research Institute of Fisheries and Oceanography (YugNIRO, Kerch), including more than 10,000 observations on water temperature, ~10,000 observations on water salinity, ~8,000 observations on dissolved oxygen concentrations, ~7,000 measurements of dissolved inorganic P (DIP) concentrations, and the same quantity of silicate (DISi) concentration determinations at standard depths down to the bottom at 25 stations of sections on the NWSH aquatory. In total, more than 40,000 oceanographic observations were analyzed. Considering the character of horizontal variability of oceanographic characteristics of water regime, the NWSH aquatory was divided into three zones: the coastal Odessa-Danube zone (A), central Karkinit zone (B), and zone of continental slope (C), including 11, 9, and 5 stations, respectively (Fig. 5.4). After 1992 for political and economic reasons, the studies conducted by YugNIRO at the long-term standard sections in the Black Sea were ceased and 45-year-long time series was interrupted (!).

The spreading and transformation of OP fields occurs mainly in the surface water layer. Therefore, the investigations of oceanographic conditions were focused primarily on regime characteristics of surface water layer both under the analysis of their mean long-term values and during the treatment of the results of individual oceanographic surveys.

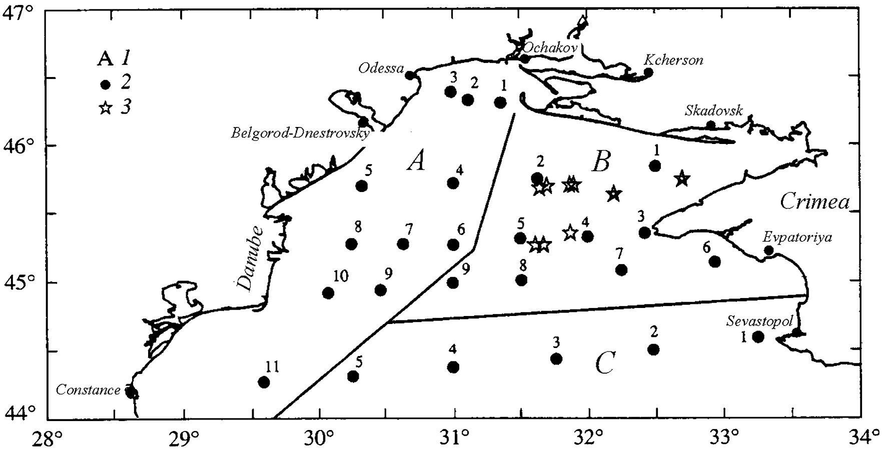


Fig. 5.4 Schematic map of areas (*1*) and stations (*2*) of the long-term (1955–1991) monitoring of environmental conditions on the NWSH of the Black Sea and location of drilling platforms (*3*) in the Karkinit Bay (Fashchuk et al. 2006a, b)

In the mean long-term context, all three areas are characterized by pronounced seasonal temperature variations from the surface to the depth of 50 m (Table 5.1). In zone A, because of the closeness to the land, the difference of mean values of this characteristic from summer to winter is maximal and amounts to 18.61 (22.99–4.38)°C; in zone B this difference decreases to 16.81 (22.72–5.91)°C, and in zone C it is minimal and equals 15.33 (22.76–7.47)°C.

The minimum values of T on the surface for the 1955–1991 period in zone A were 13.48, 19.55, 6.38, and 1.39°C in spring, summer, autumn, and winter, respectively (table of statistical characteristics is not given because of the large volume of information). The maximums in the same seasons reached here 20.12, 25.87, 13.90, and 6.44°C. In zone B, these values of T on the surface for different seasons were 12.69, 20.66, 9.39, 3.20°C and 20.07, 25.37, 15.00, 7.12°C, respectively. The respective values for zone C amounted to 12.70, 20.04, 10.14, 5.64°C and 20.48, 25.36, 14.85, 8.63°C.

In the mean long-term context, the seasonal variations in S were noted only in zone A and only down to depth of 20 m. Mean values of S vary here from 15.88‰ in the period when the river runoff is maximum (spring–summer) to 17.20‰ in autumn and winter, when the river runoff is minimum. In zones B and C, the mean values of S vary within the year from 17.70 to 18.18‰ and from 18.01 to 18.30‰, respectively.

Minimum values of S in zone A for these seasons are equal to 13.43, 19.50, 15.70, 15.56‰; the respective values are 16.04, 15.60, 16.81, 17.39‰ in zone B and 17.66, 16.16, 17.52, and 17.78‰ in zone C. The maximums of this characteristic for 1955–1991 in zones A, B, and C for seasons of the year reached 20.70, 19.74, 18.21, 18.40; 18.51, 18.11, 18.40, 18.68; and 18.50, 18.26, 18.40, 18.85‰, respectively.

Mean long-term values of dissolved oxygen content in the surface layer are similar in all three zones and vary from 5 to 8 mL/L, with maximums in winter in zone A (up to 8.14 mL/L) and minimums in all zones in summer (5.61–5.68 mL/L). The absolute minimum and maximum of oxygen concentration in the surface layer in 1955–1991 were registered in zone A and amounted to 3.66 and 9.07 mL/L, respectively (Table 5.1).

The mean content of DIP in the upper 30-m layer in all zones of the NWSH of the sea varied from 0.17 to 0.34 μg-at/L during the year. The minimums of DIP concentrations (0.03–0.06 μg-at/L) were fixed at the surface in all three zones of the shelf in summer and winter, and the surface maximum (1.23 μg-at/L) was observed in spring in zone A.

The maximums of mean long-term values of DISi concentrations in the surface layer of the NWSH were registered in winter and amounted to 19.77, 14.84, and 16.02 μg-at Si/L in zones A, B, and C, respectively. The minimums of this characteristic in zone A were noted in summer (10.49 μg-at/L), and in zones B and C they were observed in autumn (10.23 and 8.93 μg-at/L, respectively). The absolute surface maximum of DISi concentration for 1955–1991 was recorded in spring in zone A (134 μg-at/L), and its minimum (1.67 μg-at/L) was fixed in summer (zone B).

Table 5.1 Mean values of oceanographic characteristics of the Black Sea NW Shelf for 1955–1991

z (m)	T (°C)				S (‰)				O_2 (mL/L)				PO_4 (μg)-at/L				SiO_2 (μg)-at/L			
	Sp	Sum	Aut	W	Sp	Sum	Aut	W	Sp	Sum	Aut	W	Sp	Sum	Aut	W	Sp	Sum	Aut	W
Area A																				
0	16.74	22.99	10.67	4.38	15.84	15.88	17.20	17.21	6.88	5.61	6.69	8.14	0.28	0.20	0.34	0.29	19.77	10.49	14.16	17.85
10	12.79	20.25	10.78	4.42	16.94	16.51	17.33	17.68	6.84	5.42	6.64	8.18	0.24	0.21	0.29	0.26	19.11	11.93	13.59	16.92
20	8.13	12.71	11.04	4.58	17.92	17.77	17.54	18.01	6.79	5.33	6.33	7.94	0.25	0.27	0.34	0.26	21.92	18.87	13.73	16.69
30	7.16	8.34	11.13	5.53	18.18	18.18	17.90	18.22	6.65	5.84	5.21	7.70	0.28	0.26	0.30	0.24	18.94	20.70	13.93	16.25
50	6.61	6.99	8.47	6.22	18.30	18.36	18.27	18.42	6.21	4.47	4.02	7.23	0.38	0.44	0.48	0.40	19.62	23.90	15.06	21.90
Area B																				
0	16.29	22.72	12.04	5.91	17.70	17.22	17.91	18.18	6.61	5.68	6.51	7.73	0.24	0.22	0.18	0.24	14.84	12.76	10.23	16.81
10	14.45	21.23	12.07	5.89	18.77	17.62	17.95	18.23	6.75	5.70	6.52	7.74	0.22	0.22	0.18	0.21	15.00	13.50	10.84	18.17
20	11.02	14.69	12.10	5.93	18.15	18.14	17.99	18.23	7.12	6.54	6.48	7.67	0.23	0.24	0.17	0.25	16.47	15.00	11.19	18.29
30	9.14	10.07	11.97	6.27	18.24	18.22	18.13	18.33	7.17	7.05	6.37	7.58	0.25	0.23	0.18	0.25	16.88	16.91	11.41	18.19
50	7.49	7.55	9.06	6.47	18.32	18.33	18.36	18.38	6.78	6.35	5.77	7.34	0.33	0.37	0.29	0.25	19.61	24.78	17.10	18.64
75	7.41	7.438	7.388	6.42	18.51	18.68	17.74	18.50	5.91	4.38	4.39	6.16	0.50	0.60	0.44	0.43	24.83	31.79	22.30	24.92
Area C																				
0	15.90	22.76	12.58	7.47	18.01	17.69	18.14	18.30	6.61	5.64	6.56	7.38	0.23	0.20	0.21	0.24	16.02	14.38	8.93	14.97
10	14.44	21.65	12.57	7.45	18.07	17.84	18.14	18.31	6.69	5.77	6.55	7.36	0.23	0.18	0.15	0.23	15.29	15.33	9.38	15.12
20	11.93	15.67	12.41	7.43	18.14	18.06	18.15	18.30	7.05	6.71	6.57	7.31	0.26	0.19	0.15	0.27	17.71	25.12	10.22	16.00
30	9.77	10.62	11.95	7.39	18.21	18.22	18.18	18.35	7.13	7.20	6.57	7.28	0.25	0.18	0.17	0.27	18.05	16.10	10.04	17.11
50	7.99	8.13	9.45	7.29	18.34	18.37	18.33	18.40	6.90	6.74	6.33	7.15	0.33	0.23	0.23	0.31	19.55	20.09	12.09	18.07
75	7.48	7.429	8.028	7.38	18.60	18.60	18.70	18.81	5.99	5.84	5.11	5.97	0.47	0.39	0.46	0.47	24.82	25.91	20.98	24.84
100	7.651	7.70	7.834	7.71	19.12	19.24	19.42	19.21	4.10	3.61	3.11	4.26	0.75	0.79	0.97	0.77	36.64	40.78	36.07	33.47
150	8.228	8.32	8.316	8.20	20.15	20.39	20.53	20.23	1.38	1.55	0.97	1.53	1.64	1.64	2.51	1.53	61.44	62.04	71.21	58.58
200	8.52	8.60	8.609	8.56	20.93	21.13	20.92	20.87	0.65	0.36	0.43	0.38	2.40	2.15	2.97	1.81	86.12	89.00	84.47	78.64

Sp spring, *Sum* summer, *Aut* autumn, *W* winter

5.2.3 Atmospheric Transfer and Wind Currents

The types of atmospheric synoptic processes (SPs) over aquatory of the northwestern shelf change essentially, depending on season, and have the long-term cyclicity. In the 1970–1980 period the western type of atmospheric transfer over the Azov and Black Seas started to prevail over the eastern type during a year (Matishov et al. 2008) that resulted in increase in river runoff, freshening, and rise of their level.

In winter, under the influence of periodically passing Mediterranean cyclones, the cyclonic type of atmospheric circulation associated with the SW transfer of air masses, prevails here. Moreover, under the influence of the wedge of anticyclone which center at this time usually located over the western regions of the European Russia, continental air masses of midlatitudes can periodically invade the area under investigation from the north and the northeast. With that, the strengthening of NE wind up to the stormy is observed.

In summer, over most of the sea the anticyclonic type of SPs, with prevalence of low wind weather, is established. In the north of the sea aquatory this is associated with spreading of influence of the Azore High wedge here that is accompanied by establishment of fine weather. During this period the role of the radiation factor in its formation exceeds the importance of advective mechanisms, characteristic for winter.

From eight types of the synoptic processes defined for the Black Sea, the northern, northeastern and southwestern ones have the largest annual frequency of occurrence (11–13%). Its maxima for the sum of N and NE types are 25–28%. For the SW type they make 15–20% and are observed in winter. The frequency of other types of atmospheric transfer corresponding to the remaining wind directions is distributed uniformly within a year and does not exceed 8% of cases per month (Project "The Seas …" 1991).

The average duration of strong winds (more than 10 m/s) over the NWSH aquatory for a year is 1,186 h, with maxima in December–February (140–187 h). Their maximum duration makes 1847 h, with peaks from 224 to 280 h in winter months. Under the north winds, two circulations are formed on the shelf: the western anticyclonic circulation (in the Dniester–Danube interstream area) and eastern cyclonic circulation (in the Karkinit Bay), with flow velocities to 15–25 cm/s (Fig. 5.5).

Under the northeast and east winds the whole shelf aquatory is occupied by one cyclonic circulation, with velocities to 40–50 cm/s in the western part of, and to 20–25 cm/s in its eastern part. Under the southeast winds three circulations are formed here: two cyclonic ones in the centre and in the Karkinit Bay and anticyclonic circulation in the western area, with current velocities to 20–30 cm/s on the eastern shelf, and to 35–45 cm/s in the Odessa area.

Under the south winds the cyclonic circulation is formed in the west of the area, and anticyclonic circulations are developed in the east (in the Karkinit Bay), with current velocities up to 15–25 cm/s. Under the southwest winds the one

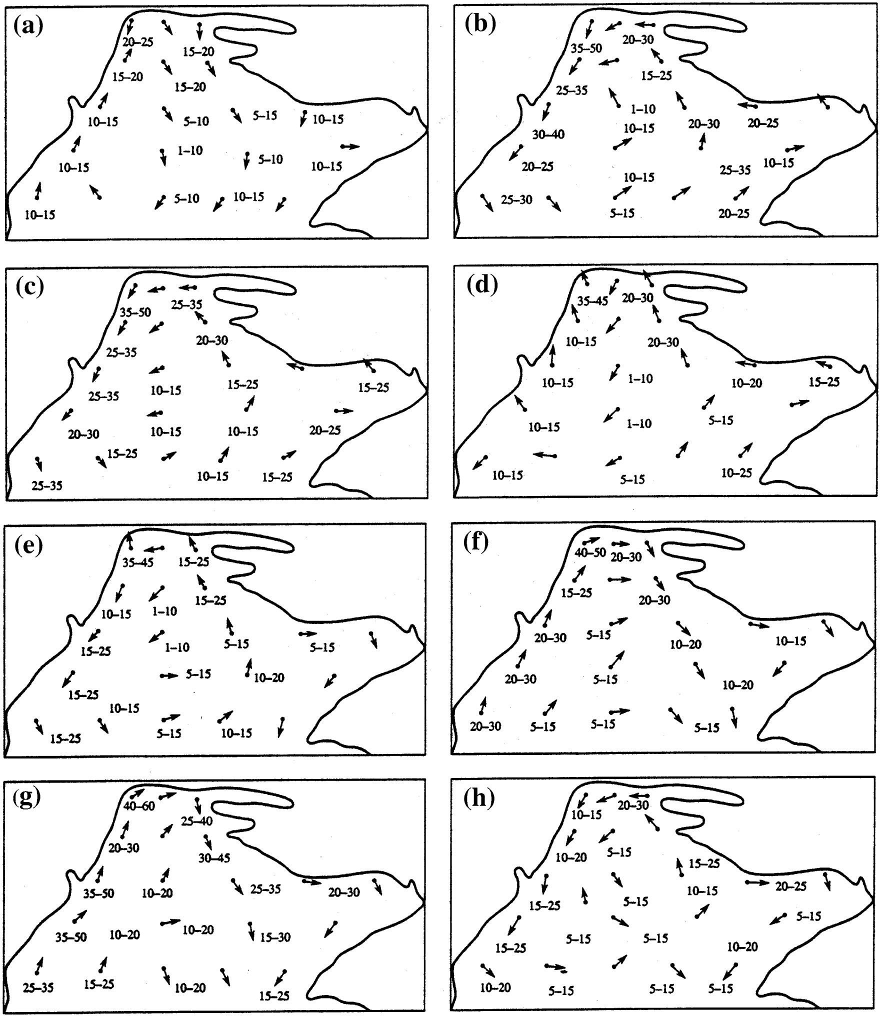


Fig. 5.5 Scheme of the depth-integrated water wind circulation, sm/sin the northwestern Black Sea (Project "The Seas …" 1991). Wind types: **a** north, **b** northeast, **c** east, **d** southeast, **e** south, **f** southwest, **g** west, **h** northwest

anticyclonic circulation, with current velocities up to 40–50 and 20–30 cm/s on the northern and western peripheries, respectively, is established on the whole shelf. Under the west winds, two anticyclonic circulations are formed in the Dniester–Danube interstream area, central part of the shelf, and also in the Karkinit Bay, with the maximum current velocities up to 35–50 cm/s along the western coast of the area. Under the northwest winds the cyclonic circulation is formed in the western area, and anticyclonic circulation is developed in the east, with current velocities to 10–15 cm/s.

5.2.4 River Discharge

During the 1923–1985 period the mean annual river discharge into the Black Sea was 340.6 km^3. From them, 79% were contributed by the rivers of the northwestern Black Sea (269.2 km^3), about 13% (43.2 km^3)—by the rivers of the Caucasian coast. The share of Turkish rivers was 7.7% (26.3 km^3) and that of the rivers of Bulgaria and Romania—less than 1%.

The maximum total runoff during this period was observed in 1970 (492 km^3), and minimum—in 1949 (246 km^3) that amounted to 145% and 73% from the long-term mean. For the Danube these values were 313 (1941) and 136 km^3 (1949), or 150% and 65% from the long-term mean (208 km^3), respectively. For the Dnieper, the maximum and minimum runoff volumes were equal to 83.2 (1933) and 23.0 km^3 (1960), or 174% and 48% from the mean long-term annual value of 47.9 km^3.

Appearing in the sea, river waters on the NWSH are localized along the shelf edge (over depths of 100–120 m), forming here the density front between shelf waters (salinity of 10–14‰) and waters of the open sea (salinity of 18–18.5‰) that prevents the horizontal spreading of polluting substances (PSs). Freshened waters form the specific stratification conditions on the shelf, when the vertical salinity gradients can reach here 4‰/m (Fashchuk et al. 1986). Moreover, an increase in river discharge results in deepening of the halocline layer and increase in depth of penetration of PSs.

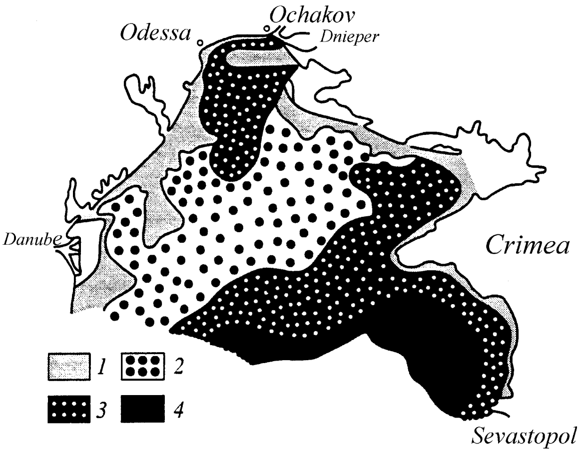
River runoff, being the main source of sea supply with sedimentary material forms, thus, its geochemical background (GChB). Now, the Black Sea receives annually 137.6 million t of suspended sediments with solid runoff. From this amount, 67.5 million t is contributed by the Danube, 38 million t—by the rivers of the Anatolian coast, more than 25 million t—by the Caucasian rivers, and only on 1–2%—by the Dnieper, Dniester, Southern Bug, the rivers of Crimea and Bulgarian coast (Mitropolsky et al. 1982).

5.2.5 Bottom Sediments and Aquatic Geochemical Landscapes

Suspended particles carried with river runoff, form the certain types of bottom deposits on the shelf (Fig. 5.6). Shell limestone and shell sands consisting mainly of mussel material prevail at the tops of relief elevations in the northwestern Black Sea and their slopes. In paleovalleys shell limestone is replaced with silty shell deposits. Shell silts are met in the Dnieper trough, in the lower part of its slope, and the bottom of trough is covered by almost pure silts. Silty deposits are characteristic also for the southern part of the Odessa depression and the Danube delta front (Fesyunov and Nazarenko 1991).

Sandy and shell limestone grounds with the low content of pellite fractions (0.3%) and organic matter (OM) (0.1–0.3%), and decreased content of microelements

Fig. 5.6 Scheme of bottom deposit types on the northwestern shelf of the Black Sea (Fesyunov and Nazarenko 1991). *1* sands, *2* shell limestone, *3* fine silts, *4* clayey mud



are typical *for the coastal zone* of the NWSH. Fine suspensions with the content of pellite fractions and OM to 20 and 1–1.5%, respectively, are deposited *in the center* of the northwestern Black Sea. The manganese, nickel and copper concentrations in deposits of such oxygen-clayey and oxygen-hydrogen sulfide aquatic landscapes increases 1.5–3 times, while in water their content decreases by factor of 1.2–2.4. These types of landscapes are characterized by the maximum concentrations of phyllophora, containing 10–20 times more such microelements as nickel, cobalt, molybdenum, and 5.5 and 1.4 times more copper and lead in ash than in bottom deposits, thus enriching bottom deposits with them after dying off. Clayey mud, with the OM content to 1.5–2%, are formed *on the outer shelf edge* (*southern area*) *and in the Kalamitsky Bay* (*eastern area*). Depending on oxidation–reduction conditions, manganese, iron, nickel, cobalt, molybdenum, vanadium are concentrated here, and iron-manganese nodules are formed also. The nickel content in deposits of these areas is, for example, 6–9 times higher than that of titan and vanadium and 2–8 times higher than the copper and manganese concentrations, compared with sands. In near-bottom waters of such landscapes the maximum (for the whole shelf) concentration of these elements, exceeding the background values 1.2–1.4 times, are observed.

Bottom deposits are the main component of aquatic landscapes (Fig. 5.7), bottom sites with homogeneous vegetation communities, geochemical conditions, and located on the homogeneous elements of relief (Khovansky and Chernousov 1989).

5.2.6 Synoptic Eddies on the Shelf Edge

The important role in formation of environmental conditions on the northwestern shelf and, in particular, intensity of advection of polluting substances from the open areas of the sea and coastal zone of the South Coast of Crimea on shoal is

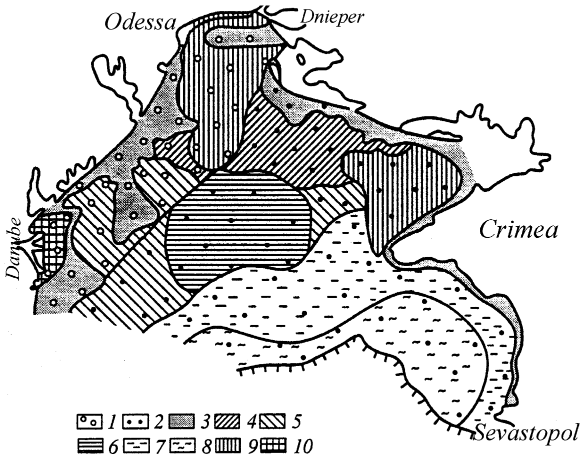


Fig. 5.7 Scheme of geochemical landscapes of the northwestern Black Sea (Khovansky and Chernousov 1989). *1* high-productive landscapes with phytoplankton biomass of 0.4–2 g/m^3, *2* medium productive landscapes (0.2–0.4 g/m^3). *Oxygen trans-aquatic landscapeson*: *3* sublimestone and limestone sands, *4* shell limestone. *Trans-accumulative landscapes on shell limestone*: *5* oxygen-clayey, *6* phyllophora oxygen-clayey. *Oxygen-hydrogen sulfide low-reduced* landscapes: *7* trans-accumulative on sublimestone and limestone fine silts, *8* accumulative on sublimestone clayey mud. *Oxygen-hydrogen* sulfide landscapes: *9* accumulative on sublimestone fine silts; *10* delta-accumulative on sublimestone aleuritic silts

played by its water exchange with these areas of the basin. One of its mechanisms is associated with the synoptic eddies forming on the periphery of the Main Black Sea Current (MBSC), stretching over the southern border (continental slope) of the shelf (Fig. 5.8).

Off the Southwest Coast of Crimea and along the continental slope of the northwestern Black Sea the presence of anticyclonic circulation was fixed from the beginning of the 1950s by indirect signs (concentrations of zooplankton and fish eaten by dolphins) (Nadezhin 1950). In the following, it was identified by hydrological data (Fashchuk et al. 1987; Latun 1989; Andrianova and Kholoptsev 1992; Moskalenko et al. 1994); by instrumental observations on currents (Panteleev and Shcherbakov 1990; Titov 1992, 1993); as a result of climatic generalizations (on season scale) of hydrophysical fields (Yeremeev et al. 1991); by data of remote (satellite) sounding of sea surface temperature (Grishin et al. 1993); by results of numerical modeling of synoptic eddies in the Black Sea (Demyshev and Korotayev 1994). As a result, its following characteristic features were revealed:

- on maps of dynamical topography the anticyclonic circulation in the area under consideration can appear almost in any time of the year (see Fig. 5.8);
- according to hydrological data, the maximums of its development are observed in the flood periods (spring, autumn) and in periods of cyclonic type of weather (winter) with the SW atmospheric transfer over the sea aquatory;

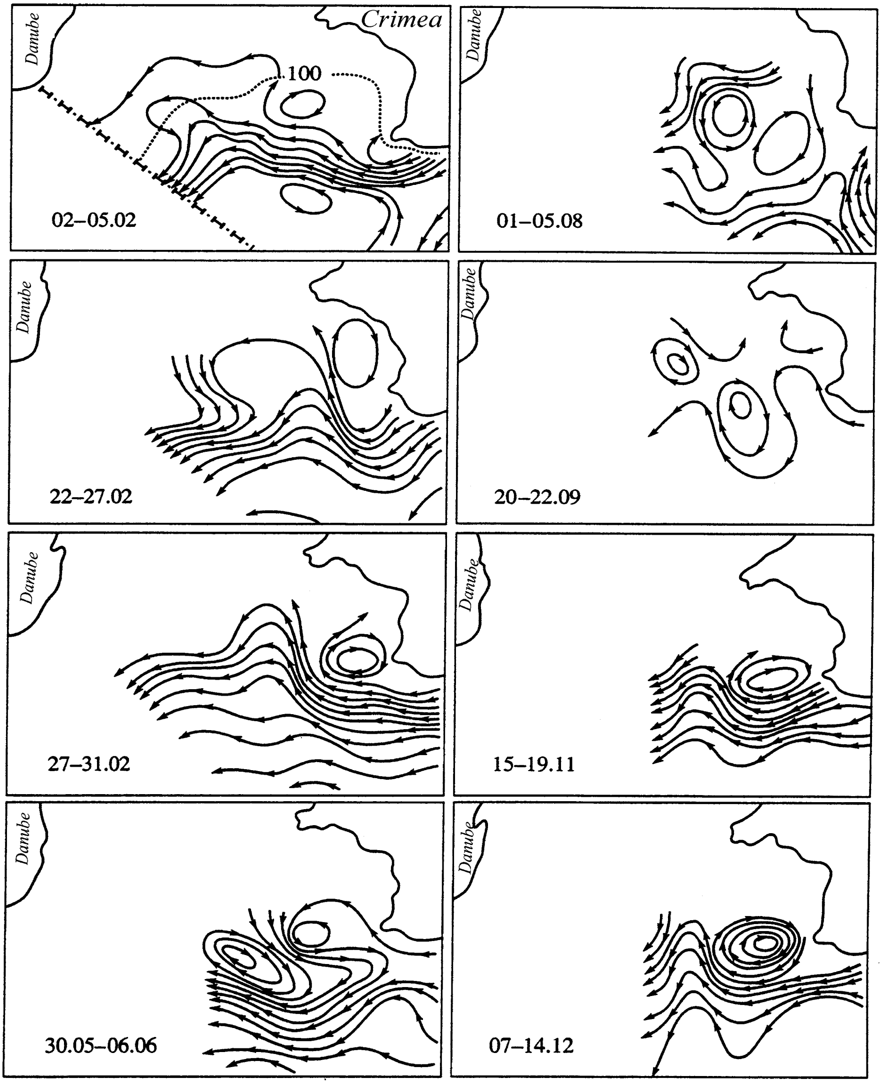


Fig. 5.8 Geostrophic water circulation at depth of 100 m along the northwestern shelf edge in 1987. The *left part* of upper figure shows the border of territorial waters of Ukraine and Romania

- according to instrumental observations, speed of horizontal displacement of synoptic eddy is 10–15 cm/s (8–10 km/day), and time interval between consecutive eddies can reach 2, 6, and 12 days.

The existence of such phenomenon affects essentially the intensity of water exchange of the NWSH with the open sea and, correspondingly, the rate of removal of oil products from the shelf zone.

- diameter of circulation can reach 30 km, current velocities on its periphery—30 cm/s, and depth of penetration—300 m, with its maximum value of 1,000 m (spring–summer season, 1988).

5.3 Background of Environment Pollution on the NW Shelf

The aquatory of the northwestern shelf of the Black Sea and territory of its watershed basin practically always and especially in the 1960s–1980s were an arena of intensive economic activities. Now, because of the known political and economic circumstances, the anthropogenic press on the shelf ecosystem decreased substantially. Nevertheless, it remains the most exploited region of the Black Sea.

The most common forms of economic activities in the watershed basin territory, determining the level of anthropogenic load on the shelf ecosystem, are: disposal of waste waters from industrial plants and household effluent of watershed cities in the river net and directly into the sea, and application of various types of chemical fertilizers and technical agents in agricultural production. Other forms of economic activities on the shelf aquatory are associated with intensive navigation, marine extraction of sand and natural gas, dumping of grounds as a result of dredging; trawl fishery (see Fig. 1.13).

5.3.1 Economic Activities on the Watershed Territory and Shelf Aquatory

There are 11 industrial-municipal agglomerations at the coast of the northwestern Black Sea, which provide the main discharge of sewage waters into the sea. From the Danube mouth in a clockwise direction they are located in the following order: the Tatarbunary, Belgorod-Dniester, Odessa, Ochakov, Mikolaiv, Kherson, North Crimean, Yevpatoria–Saki, Sevastopol, Feodosiya, and Kerch agglomerations.

In Odessa, Sevastopol, and Mikolaiv, the machinery and the instrument making industry polluting sewage waters of production with alkalies, acids, suspended matter, oils, and salts of heavy metals, are developed. The chemical and inorganic manufactures of the Odessa and North Crimean agglomerations dispose inorganic compounds of nitrogen and phosphorus, synthetic surfactants (SS) phenols, mercury, arsenic into the sea with sewage waters. The food-processing industry enterprises in these zones pollute the sea with organic compounds: proteins, fats, carbohydrates. Waste waters of municipal sewerages of Odessa, Sevastopol, Mikolaiv, Kherson contain the huge amounts of suspended substances (33–200 MACs), oil products (1.5–75 MACs), nitrates, and nitrites.

From 1166.4 million m^3 of collector and drainage waters and operation wastes received by the sea annually from the large irrigating systems of Ukraine, the share

Table 5.2 Comparative estimation of volumes of polluting substances disposed into the northwestern Black Sea (t) with waste water (Belyaev et al. 2001)

Type of polluting substance	Region			Total	Exceedence level of concentration in waste water, compared with river waters (times)
	Odessa	Sevastopol	Karkinit Bay		
Suspended OM	9,768	5,056	8,692.3	23,516.3	4.8
Ammonium nitrogen	1,905	1,090	1,253	4,248	16.3
Nitrate nitrogen	643	632	978	2,253	1.2
Nitrite nitrogen	22.5	12.6	105	140.1	2.9
Total phosphorus	649.8	272.5	582.7	1,504.8	2.5
Detergents	55.2	47.2	34.5	136.9	4.3
Oil products	28.5	22.9	14	65.4	2.9
Phenols	2.7	1	No data	3.7	5.5
Annual volume of waste water (km^3)	0.452	0.316	0.765	1.533	

of the Crimea, Odessa and Kherson Regions is 945.5 million m^3/year, from which 62% (588 million m^3) is disposed in the Karkinit Bay of the northwestern Black Sea. Annually, it gives to the bay: 11.7 t of heavy metals (Mn, Cu, Pb, Zn), 34.5 t of SS, 2.,3 thousand t of inorganic forms of nitrogen, more than 0.5 thousand t of phosphates, more than 1,000 t of organic matter, about 9,000 t of suspended matter (Belyaev et al. 2001).

Annually (1980–1989), every 30% of total volume of waste water making about 1 km^3/year, were disposed into the Black Sea with the Danube and Dnieper discharge (Fashchuk et al. 1995). According to present estimations, disposal of waste water into the northwestern sea is: 0.452 km^3/year in the Odessa area and 0.765 km^3/year in the Karkinit Bay area (Table 5.2). These waters bring here about 20 thousand t of suspended organic matter, 3,000 t of ammonium nitrogen, about 2,000 t of nitrates, more than 1,000 t of total phosphorus, about 100 t of detergents, 65 t of oil products, and to 3 t of phenols (Photo 5.5).

Inorganic Compounds of Phosphorus and Nitrogen Almost the whole discharge of these most mass types of polluting substances run into the sea with waters of the Danube and Dnieper (about 80 and 600 thousand t, respectively). The Danube contribution for both characteristics is 12 times higher than that of the Dnieper. The discharge of nutrients from the coast makes less than 2% of the total, from which the share of the northwestern sea is 10–15%.

It is established that the Black Sea receives 60% and 36% of NH_4^+ (about 9,000 t/year) with waters of the Danube and Dnieper, respectively, about 5% are disposed by the coastal enterprises. From the latter, only 4% enter the northwestern Black Sea, the remaining amount of ammonium nitrogen is supplied by sewage of the Crimean and Caucasian enterprises.

According to data obtained in 2001 (Garkavaya and Bogatova 2001), with river discharge (194 km^3) the northwestern Black Sea receives annually: about 300 thousand t of inorganic and 700 thousand t of organic nitrogen, 24 thousand t of phosphates, 31 thousand t of organic phosphorus, 700 thousand t of silicon.

Photo 5.5 Today the contribution of the Odessa port and river discharge to pollution of the northwestern shelf of the Black Sea was added by marine gas production. Odessa port from ISS

According to calculations and estimations of other authors, the whole Black Sea receives today from 8.7 (The Black Sea … 1997) to 15 thousand t (Edelshtein 1998) of phosphates with municipal sewage of coastal countries.

In recent years it was established also that atmospheric precipitation (20–25 km^3/year) served as an additional source of eutrophication of surface water layer on the northwestern shelf of the Black Sea. Today this factor produces about 50 thousand t of ammonium nitrogen, to 15 thousand t of nitrates, 23 thousand t of organic nitrogen, 160 thousand t of organic matter for the area under investigation that is comparable to their discharge with the Dnieper waters. Moreover, it emerged that in the period of summer hypoxia development on the northwestern shelf, within a month, up to 50–80 thousand t of ammonium nitrogen, 10–17 thousand t of phosphates, and 40–90 thousand t of silicon was released from bottom deposits to the water (Garkavaya and Bogatova 2001).

Oil Hydrocarbons (OHC) During 1980–1989 on the average 80 thousand t of oil products entered annually the Black Sea (approximately 65% from them—with the river discharge; at that, the share of the Danube was 3.5 times larger than that of the Dnieper). From 1.5–2 thousand t of total amount of OHC disposed annually into the sea with waste water of the coastal enterprises, the Odessa area accounts for 30%.

Synthetic Surfactants (SS) From 20 thousand t of detergents disposed now annually into the sea, 34% are brought by Danube waters, 26%—by the Dnieper, and 40%—by industrial waste waters of the coast. The Odessa area accounts for

98% of the total SS supply with industrial waste waters that is by a factor of 1,000 larger than the load of the Krasnodar Territory coast (which is the second by the SS disposal) with these polluting substances.

Phenols During the last decade the Black Sea received annually up to 1,000 t of phenols with river discharge (80% and 20% from the Danube and the Dnieper, respectively). There is only a few data on their disposal with industrial waste waters.

Organochlorine Pesticides (OCP) More than 20 and 1 t of OCP is supplied annually into the Black Sea with Danube and Dnieper waters, respectively. Their other source is associated with collector and drainage waters (CDW) of irrigating systems of rice fields. The Karkinit and Dzharylgach Bays of the northwestern Black Sea receive annually up to 1 km^3 of CDW, the total volume of all industrial waste waters from the coast, from the Danube mouth to Batumi.

Heavy Metals (HM) The different authors (Patin 1979) rank microelements by their toxicity approximately in the following order: mercury, copper, lead, cadmium, chrome, zinc, arsenic. The main anthropogenic of these toxicants for river and sea waters are associated with industrial manufactures.

Mercury The compounds of this toxicant are contained in waste waters of the enterprises producing dyes, chemicals, insecticides and fungicides, pharmaceuticals, and some explosives.

Copper is disposed into the water basins with chemical and metallurgical wastes, at production of algaecide reagents for killing of algae, and with mine waters.

Lead enters river and sea waters with waste waters of ore-dressing plants, some metallurgic plants, chemical production and mines, and at coal combustion and application of tetraethyl lead as detonator in motor fuel.

Cadmium Its sources for water basins are also associated with waste waters of ore-dressing plants, some chemical manufactures, lead and zinc plants, and mines.

Chrome is supplied to the rivers and seas with waste waters of electroplating shops of metallurgy and machine-tool manufactures, automobile and aircraft factories, painting shops of textile plants, tanneries, and chemical plants.

Zinc appears in the surface layer with waste waters of manufactures of parchment paper, mineral paints, synthetic fibers, and from ore-dressing plants and electroplating shops of many other productions.

Arsenic is disposed into the water basins with waste waters of ore-processing plants, wastes of dye production of tanneries, chemical and metallurgical factories, and factories producing insecticides and pesticides.

According to data of the International Program for Monitoring and Water Quality (Buijs 1991), in 1988–1989 the Danube brought annually on the average 55 t of mercury, 500 t of cadmium, 900 t of copper 3,000 t of lead, and 4,500 t of manganese to the Black Sea.

From the segmental information of Yearbooks of the Hydrometeorological Service, it follows that during last decade the sea received from 10 to 100 t of copper, aluminium, and nickel with industrial waste waters. The information for other metals is practically not available from this source. In the Mediterranean Sea, the annual industrial disposals of HM are: 10 t for mercury, 1,400 t for lead, 950 t for chrome, and about 5,000 t for zinc (Izrael 1984) that several times exceeds their natural supply with solid runoff.

In the process of ground dumping, the total annual supply of Cr, Zn, Cu, and Pb to the Black Sea ranges within hundreds of tons (Sevrikova 1988; Sevrikova et al. 1991; Semenov and Dolzhenko 1993). Under the development of marine oil and gas fields, such toxic HM as chrome, lead, copper enter the water (Semenov and Pavlenko 1991) but their exact amount was not estimated to the present day.

5.3.2 Index of Anthropogenic Load on Water Resources of the Watershed Basin

The specialists from Institute of Geography of the Russian Academy of Sciences developed the index allowing to combine the hydroclimatic and social features of the watershed basin territory into the single criterion (Koronkevich 1995). It represents the ratio of population density to the value of mean annual runoff depth from the watershed territory. This index, thus, shows how many inhabitants fall on the unit of watershed water resource volume, i.e. it allows calculating an indirect factor of ecological role of watershed territory for marine ecosystem.

The calculations for the Black sea watershed basin (Fashchuk 1998) and, in particular, for the watershed territory of the northwestern shelf allowed to establish that the index values ranged from less than 1 to 2,000 people/10^5 m^3 of freshwater runoff (see Fig. 1.25). By watersheds of the main rivers of the northwestern sea it is distributed as follows:

5.3.2.1 The Danube Watershed Territory

In this zone, the maximum values of load are observed in the territory of Czechia and Austria (100–200 people/10^5 m^3), Hungary (up to 750 people/10^5 m^3), and Romania (up to 2,000 people/10^5 m^3). The regions of high index values (from 100 to 500 people/10^5 m^3) are located in the areas of Brno and Vienna cities, respectively, occupy almost the whole territory of Hungary and the Romanian zone of the watershed in the Danube downstream, where the values of anthropogenic load on water resources do not fall below 250–300 people/10^5 m^3. On the periphery of the Danube watershed (Germany, the western Austria, former Yugoslavia) and in the Carpathians area (Slovakia, western regions of Ukraine, Romania) in most cases less than 10 people fall on 10^5 m^3 of water.

The distribution pattern of this index in the Danube watershed territory coincides completely with the similar pattern for the mean annual runoff (see Fig. 1.20) and to a lesser degree—with population density pattern (see Fig. 1.22) *that shows a prevailing role of natural hydroclimatic factors at the formation of regime of anthropogenic load on water resources here, compared to the social factors.*

5.3.2.2 The Dniester, Southern Bug, and Dnieper Watershed Territory

In this territory, the values of the index of anthropogenic load on water resources range from 1–10 to 750 people/10^5 m^3. Its largest values occupy more than 1/3 of watershed area and are noted in the Ukrainian zone, in the watershed territories of lower reaches of these: practically in the whole territory of Odessa (with an extremum in the 30-km zone around Odessa), in the southern half of Mikolaiv, Dnepropetrovsk, and in the west of the Zaporizhia Regions. The high values (250–300 people/10^5 m^3) are noted also in the watershed areas of the middle reaches of the Dniester, upper reaches of the Southern Bug and Dnieper: the eastern Chernivtsi, southern Khmelnytskyi, whole Vinnytsia and Cherkasy Regions, the central Kiev (including city of Kiev) Region. Besides, the local maxima are located on the border of the Sumy and Poltava Regions.

For another 1/3 of this watershed territory, including the northwestern half of the Lviv Region, the Ternopil, central parts of the Chernivtsi, Khmelnytskyi, Zhytomiy, and Kirovohrad Regions, the north of the Odessa, Mikolaiv, Dnipropetrovsk, and Sumy Regions, and the southern halves of the Chernihiv, Kiev and Poltava Regions, the values of the index of anthropogenic load on water resources amount to 100–200 people/10^5 m^3.

5.3.3 Index of Potential Environmental Threat of Coastal Industrial Productions for Shelf Ecosystem

The criterion of potential ecological threat (PET) of coastal industrial production for the marine aquatory and main rivers is taken as the sum of ratios of concentration of toxic polluting substance in waste waters to its MAC in the marine environment, i.e., the total MAC value of all investigated conservative toxicants, containing in industrial waste waters of a corresponding city (see Sect. 1.7.4).

The results of calculation of the index of the PET and its structures for the most mass toxicants in big cities of the Black Sea watershed basin allowed estimating, disposal of which toxicant and in what city can be the most dangerous if waste waters do not pass through the corresponding treatment, and, in this context, to compare the cities under investigation (see Fig. 1.26).

The maximum values of the PET index (10^6–10^7) are noted in three cities, Odessa (12.68 million), Kiev (8.36 million), and Dnipropetrovsk (8.22 million). In three cities (Belgrade, Cherkasy, Mikolaiv) the PET values are within the range of 500,000–1,000,000.

By oil hydrocarbons the most dangerous industrial productions for the northwestern shelf of the Black Sea are located in *Sevastopol* (their share in structure of the PET index here equals more than 40%). The contribution of this toxicant to the total PET value in *Burgas, Vienna, Mogilev, Kherson* is also significant and exceeds 20%. By detergents, *Varna and Constanta*, where the share of these toxicants reaches 8%, stand out from all cities under investigation. The contribution of phenols to the value of the PET index prevails in *Odessa* (98%), *Linz* (55%), *Vienna* (30%), *Budapest* (53%), *Belgrade* (76%), *Tiraspol* (39%), *Mogilev* (34%), *Kiev* (95%), *Cherkasy* (74%), *Dniprodzerzhynsk* (46%), *Dnipropetrovsk* (97%), *Zaporizhia* (63%), *Nikopol* (68%), *and Mikolaiv* (66%). The industrial waste waters of *Sevastopol* (32%), *Varna* (63%), *Constanta* (63%), *Bratislava* (27%), *Tiraspol* (23%), *Mogilev* (20%), *Kremenchuk* (52%), *and Dniprodzerzhynsk* (46%) are characterized by the considerable copper content. By lead only Bratislava (14%) stands out from all cities under investigation. By chrome the essential contribution to the PET index value is noted in *Sevastopol* (22%), *Burgas* (33%), *Bratislava* (28%), *Budapest* (31%), *Tiraspol* (24%), *Kremenchuk* (29%), *and Kherson* (55%). None of the watershed cities is marked by high zinc concentration.

5.3.4 Interannual Variability of Polluting Substance Supply

5.3.4.1 Compounds of Phosphorus and Nitrogen

The analysis of the results about the scales of polluting substance supply onto the shelf for the 1980s in parallel with the literary data (Saadzhan, 1984) for the previous period of time showed that in comparison with 1958–1959 the total discharge of N_{tot} with the Danube and Dnieper waters increased 8 times, discharge of P_{tot} with waters of Danube—10 times, and in the late 1970s the Dniester delivered these substances 2 times more than in 1963–1974.

Against such a growth of river water load with phosphorus and nitrogen compounds, within the decade under investigation (in the second half of the 1980s) the almost twofold reduction of P_{tot} discharge into the sea with the Danube waters (from 85 to 47 thousand t/year) and, on the contrary, also an almost twofold increase in its volume for the Dnieper (from 3,690 to 7,150 thousand t/year) were noted. During the same time, waters of these rivers began to bring 5–8 and almost 17 times less ammonium nitrogen, respectively. As a result, the disposal of this polluting substance with the Danube runoff decreased from 16 to 2–3, and that with the Dnieper waters—from 17 to 1–2 thousand t/year. The supply of N_{tot} with Dnieper runoff practically was not changed, and its disposal with the Danube waters in 1989 г was 4 times less than in 1987.

By the end of the 1980s the total annual supply of P_{tot} into the sea with waste waters of coastal plants was reduced 3–5 times (from 600–700 to 100–200 t), while the disposal of nitrogen compounds from this source remained practically unchanged (about 1,000–2,000 and 200–400 t annually).

By 2001 in the Danube offshore zone the concentration of ammonium nitrogen decreased 2–3 times, that of nitrates—1.5–2 times, phosphates—1.5–3 times. But the content of organic nitrogen compounds increased 2–4 times, and such tendency continues (Garkavaya et al. 2000; Garkavaya and Bogatova 2001).

5.3.4.2 Oil Hydrocarbons

By the end of 1980s the annual volumes of oil product disposal with the Danube runoff were reduced 2.5 times (from 55 to 22 thousand t, on the average), and with the Dnieper runoff—1.5 times (from 13 to 9 thousand t). For the same period their total supply into the basin with waste waters of the coastal plants from Odessa to Batumi decreased by 60%.

5.3.4.3 Synthetic Surfactants

By the end of the 1980s the volumes of SS disposal with waters of the Danube and Dnepr decreased 2.5 and 30 times, respectively, and their annual supply into the sea with industrial waste waters of the whole coast decreased more than 30 times (from 6,500 to 200 t, on the average).

5.3.4.4 Phenols

Very irregular data available now does not allow making any correct conclusions on the character of interannual variability of the Black Sea load with this pollutant type.

5.3.4.5 Organochlorine Pesticides

For the second half of the 1980s the mean annual supply of OCP with the Danube runoff was reduced 7 times (from 42 to 6 t). For the Dnieper this factor did not change and remains at the level of 0.6–0.7 t.

5.3.5 Present Level of Water Pollution

5.3.5.1 Phosphorus and Nitrogen Compounds

During the 1984–1989 period the mean annual concentration of P_{tot} in waters of the Danube and Dnieper were 361 and 117 μg/L, N_{tot}—2,843 and 780 μg/L, and NH_4^+—42 and 101 μg/L, respectively. In the Danube influence zone the mean annual content of total phosphorus and nitrogen in sea water amounted to 129 and 3,017 μg/L, respectively, and in some years in the summer their concentrations exceeded essentially the mean annual values. So, in August, 1986 off the Danube mouth and in the area of Odessa port the content of P_{tot} reached 660 and 300 μg/L that was 4–5 times higher than the norm. In the summer, 1986–1987 the maximum concentration of N_{tot} at the surface and in the near-bottom water layer of the

Danube offshore zone reached 12,500 and 13,500 μg/L, i.e., almost 10 and 20 times above the mean annual values, and on the outer road of Ochakov, in the Sevastopol Bay, and port of Odessa its content at this time was 3–5 times above the norm (Fashchuk et al. 1995).

In 1994–1997, in the Danube offshore zone the phosphate concentration in the surface layer (to 84 μg/L) were 3–4 times lower than those by data of the 1970–1990 in 3–4 times. Compared to the indicated period, the content of organic phosphorus decreased here also, from 25–129 to 14–61 μg/L; that of ammonium nitrogen—from 500–700 (with maximum of 1,500 μg/L) to 20–72 (maximum of 354 μg/L), nitrites—from 50 to 14 μg/L for averages, nitrates—from 610 to 136 μg/L. At the same time, the concentration of organic nitrogen in the Danube offshore zone can change today from 108 to 15,950 μg/L (extreme for sea water) due to intensive development of production processes during the spring–summer period (Garkavaya et al. 2000; Sovga et al. 2000).

5.3.5.2 Oil Hydrocarbons

Their mean annual content in waters of the Danube and Dnepr in 1980–1990 was 187 and 245 μg/L, respectively. The maximum mean annual values, 340 and 430 μg/L, were registered here in 1985. These values exceeded the maximum allowable concentration (MAC), amounting to 50 μg/L, 6.8 and 8.6 times.

The spatiotemporal variability of oil hydrocarbon concentrations in coastal waters of the Black Sea is very considerable. Its general regularities are an increase in concentration from winter to summer and excess of oil hydrocarbon content in the surface layer (by 20–40%), compared to the near-bottom layer. In waters of the northwestern Black Sea the maximum concentration of oil products are observed in June–July. During the 1983–1989 period the coastal zones of Odessa and Sevastopol were the most polluted with oil products areas of the Black Sea. The maxima of oil product content in coastal waters amounted here to 1,000 and 3,270 μg/L, respectively, or 20 and 65 MACs.

The mean annual content of oil products in waters of the Danube offshore zone in the late 1980s came up to that in the areas of Yalta, Anapa, and Pitsunda, though, for example, in 1989, its values exceeding MAC on the average 3 times, and by the maximum—28 times, were noted here.

According to data obtained in 1998–1999, the high concentrations of oil products persist today near Cape Tarkhankut (140–160 μg/L, or 2.5–3.3 MACs) (Shchekaturina et al. 2002) and in the Danube coastal area (up to 220 μg/L, or more than 4 MACs) (Chugai and Safranov 1999), and in the Dniester and Dnieper offshore zones they do not exceed the norm.

Comparing the obtained data to the results of studying of the level of water pollution with oil products in other regions of the World Ocean (Nemirovskaya 2004), it may be concluded that even the mean weighted concentration of oil products in water of the northwest shelf of the Black sea exceed almost tenfold their content in the surface layer of any region of the World ocean, except for the

Northwest Indian (Arabian and Red Seas, waters of Oman and Aden), where the oil pollution background is close or exceeds several times that of the Black Sea.

5.3.5.3 Synthetic Surfactans

Now the SS concentrations in the Danube runoff reach or slightly exceed MAC (100 μg/L), and in the Dnieper they are 4 times below the norm. Their lowest values are registered in waters of the Danube offshore zone and off the Sevastopol coast (0.4–1 MAC). The maximum SS concentrations for the whole sea are noted in its northwestern part. Their mean annual values reached 3–5 MACs here, and in the Odessa Bay and on aquatory of Odessa port in 1988 the anomalies exceeding the norm 18 and 32 times, respectively, were fixed. Comparing these results to the sporadic data on the SS content in waters of other regions of the World Ocean (Kalmakov and Tkalin 1986), it may be concluded that the level of sea shelf pollution with detergents is 10 times higher than, for example, in the Pacific Ocean.

5.3.5.4 Phenols

Now the mean annual concentrations of phenols in the river runoff of the northwestern Black Sea exceed the maximum allowable concentration (1 μg/L) 4–5 times. The coastal aquatories of the northwestern sea are the most polluted with phenols. In the areas of the Karkinit Bay and Ochakov their water content may reach 17–18 MACs, and in the Odessa zone, at the mean annual concentrations exceeding MAC 14–16 times, in 1988 its maximum (52 MACs) was fixed that became a reason of closure of coastal beaches.

5.3.5.5 Organochlorine Pesticides

In 1979, by the decision of the 14th European Symposium on Protecting Sea Life, OCP are recognized as the most dangerous pollutant of water basins among the mass toxicants. There is no MAC in sea water for this type of toxic chemical. Now in the Danube offshore zone OCP are practically absent. In the open areas of the northwestern Black Sea the level of surface water pollution with OCP does not exceed 2–3 ng/L, while in Odessa and Sevastopol coastal waters, and in the Karkinit Bay the pollution with OCP is maximum for the sea. The mean weighted concentrations of pesticides can reach here 58, 21, and 17 ng/L, with their mean annual values of 24, 12 and 10 ng/L, respectively.

5.3.5.6 Heavy Metals

By their threat to vital functions of marine organisms, HM are the second after pesticides (Table 5.3).

Table 5.3 Content of heavy metals in water (μg/L) and bottom sediments (μg/g of dry weight) in the Danube, Dniester, and Dnieper offshore zones in November, 1998 (Chugai and Safranov 1999) (numerator—fluctuation range, denominator—mean value)

HM	Danube		Dniester		Dnieper	
	Water	Sediments	Water	Sediments	Water	Sediments
Cd	(0.1–0.4)/0.18	(0.06–0.79)/0.41	0.1	0.2	(0.1–0.3)/0.23	(0.16–0.39)/0.26
Pb	(8.5–28.6)/14.4	(3.35–41.2)/20.14	12.5	12.7	(8.5–47.9)/21.8	(7.9–29.2)/19.9
Zn	(5.9–29.7)/14.5	(16.5–84.6)/56.29	3.5	30	(4.7–46.6)/23.4	(23.9–64.4)/49
Cu	(2.4–9.8)/4.9	(6.93–94.4)/50.33	6.1	12.6	(1.0–4.4)/2.2	(7.5–31.7)/22.1
Ni	(3.7–9.3)/5.5	–	3.6	–	(2.9–7.0)/4.8	–
Cr	(0.3–6.5)/2.5	(9.34–104.0)/63.23	1.0	34.5	(0.6–5.0)/2.4	(19.7–99.0)/65.8
Hg	(0.01–0.04)/0.02	(0.035–0.413)/0.194	0.01	0.058	0.01	(0.025–0.054)/0.036

5.3.5.7 Mercury

In 1987–1990, the concentrations of this microelement in surface waters of the Black Sea ranged from 17 to 58 ng/L, with the maximum of 580 ng/L in the area of the Dnieper-Bug Liman, 272 and 209 ng/L in the Dnieper and Danube offshore zones, respectively, that exceeds MAC (100 ng/L) approximately 2 times.

5.3.5.8 Copper

Compared to ocean waters, the copper concentrations in the Black Sea are almost 30 times higher. Their values range here from 0.4 to 66.4 μg/L.

5.3.5.9 Lead

The content of this microelement in Black Sea can change from 0.3 to 27 μg/L that by the upper limit is 65 times higher than it was observed in the ocean but 3 times lower than in the Mediterranean Sea (Patin 1979).

5.3.5.10 Zinc

The fluctuation range of zinc concentration observed in Black Sea waters in the 1960s–1970s, was 1.2–42 μg/L that by the maximum value was 3 times higher than in the ocean, 5 times higher than in the Baltic Sea, and 2 times higher than in the Mediterranean Sea (Patin 1979).

Thus, in the early 1990s the mean values of HM content in surface coastal waters of the Black Sea were within MAC for fisheries waters. With that, their maximum values can exceed the norm 15 times by mercury, 10 times by copper, 3 times by lead, 15 times by zinc, and 6 times by chrome.

According to data obtained in 1998, the 3-, 1.25-, and 5-fold excess of MAC by lead at the surface in the Danube, Dniester, and Dnieper offshore zones, respectively, and the 2- and 1.22-fold excess of MAC by copper in the Danube and Dniester coastal areas were noted. In the Danube and Dnieper offshore zones the chrome content in water reaches 6.5 and 5 MACs, respectively (Chugai and Safranov 1999).

5.3.6 Assessment of Ecological Situation for Sea Water

To conclude the study of the present water pollution level on the northwestern shelf of the Black Sea, it seems appropriate to note that according to Methodical Instructions on Identifications of Zones of Ecological Disaster developed at Institute of Geography of the Russian Academy of Sciences (The criteria … 1992), under *critical* ecological situation the water content of oil products, SS, phenols, mercury, and copper exceeds 10 MACs, in case of *crisis* situation—2 MACs, and at *relatively satisfactory* situations the content of these toxicants in sea water should be less than MAC. For pesticides, the similar gradations are more than 10 μg/L, 1–10 μg/L, and 10^{-3}–10^{-2} μg/L, respectively.

By the content of oil products, the ecological situations in waters of the northwestern Black Sea in the early 1990s were *catastrophic* (more than 10 MACs) but by the average values they were *crisis* (up to 2 MACs). *By the detergent content* in the northwestern Black Sea in extreme cases the situation was also classified as *catastrophic* (more than 10 MACs) but by the average values it was *crisis*. *By phenols* even for the average concentrations the ecological situation on the shelf was assessed as *catastrophic* (more than 10 MACs). *By pesticides* the ecological situation in the Sevastopol area and northwestern Black Sea remained *crisis* (1–10 μg/L) both for the extreme and average concentrations of these pollutants.

According to assessments made by specialists of the Scientific Centre of Sea Ecology of Ministry of Ecological Security of Ukraine, in 1998, due to reduction in production the ecological situation in the area under investigation improved substantially (Photo 5.6).

By hydrochemical indicators, surface waters of the near-mouth area of the Danube began to be qualified as *very clean* (oxygen, ammonium, nitrates), *clean* (phosphates), *fairly clean* (nitrites), and *low polluted* (pH). In the Dniester offshore zone they were *very clean* (oxygen), *clean* (ammonium) and *low polluted* (by nitrites, nitrates, pH). In the Dnieper-Bug area by the dissolved oxygen and nitrates content water was *very clean*, by the percentage of oxygen saturation, content of nitrites and ammonium ions it was *clean*, by the phosphate content—*fairly clean*,

Photo 5.6 After suspension of most of producing units at the coast of the northwestern Black Sea shelf, in the late 1990s by hydrochemical indicators the ecological situation here improved substantially (Photo by author)

and by the pH value—*low polluted*. However, it should be noted that now in the near-bottom layer of the northwestern Black Sea, as in the 1980s, the hypoxia phenomenon and hydrogen sulfide zones develop almost annually in the summer period, resulting in mass kill of bottom organisms (Berlinsky et al. 2001; Khutorny 2001).

By the oil product content the water quality in the Danube offshore zone is estimated today as *moderately polluted*, and that of the Dniester and Dnieper—as *fairly clean*. Waters of the Danube and Dniester areas are qualified as *clean* and *fairly clean* by zinc, chrome, mercury, cadmium, and nickel. Only by values of lead and copper concentrations they are characterized as *low polluted*. In the Dnieper-Bug area waters are *low polluted* by zinc and *moderately polluted* by lead only.

5.3.7 Dynamics of Oil and Chemical Water Pollution Level

5.3.7.1 Phosphorus and Nitrogen Compounds

The analysis of the literary data shows that by the beginning of 1980s the concentrations of inorganic forms of phosphorus and nitrogen in river waters of the northwestern Black Sea increased 5–7 times, compared to 1958–1959, and in 1984–1989 the contents of total and ammonium nitrogen in Danube waters were 1.5 and 7 times higher than in 1980–1985 (Zaitsev 1992).

The upper limit of phosphate and nitrate concentrations in waters of the northwestern Black Sea increased from 0.65 and 7 μg-at/L in 1954–1960 (Almazov 1968; Dobrzhanskaya 1960) to 12 and 35 μg-at/L in 1978–1984, respectively (Zenin and Zaitseva 1989). According to the same authors, in 1978–1982 the water content of P_{tot} and N_{tot} in the Danube influence zone, amounted to 70–80 and 1,000–2,000 μg/L, respectively, exceeded the similar values observed here in the early 1950s more than 100 times. By the end of the 1980s these values increased 1.8 and 1.5 times more.

5.3.7.2 Oil Hydrocarbons

Compared to data obtained in 1975–1985 (Keondzhyan et al. 1990), the maximum concentration of OHC in the Dnieper offshore zone and the Karkinit Bay almost did not change in 1989, while in the Sevastopol area they increased 50 times. From the second half of the 1980s, the mean annual content of oil products in the Danube offshore zone decreased considerably but in 1989, for example, their mean annual concentration in this area increased again up to 160 μg/L (3 MACs), and the maximum values exceeded the norm 28 times.

5.3.7.3 Synthetic Surfactants

By the results of our analyses, by the end of the 1980s the SS concentration in Danube and Dnieper waters decreased approximately 1.5–2 and 10 times, respectively. Obviously, for this reason by that time waters of the Danube offshore zone and Sevastopol coast cleaned themselves largely from detergents, their concentration in the Dnieper offshore zone decreased 10–20 time (to the MAC level), though for example, in 1986 this indicator exceeded the norm here 9.6 times.

Against such an improvement of sea water quality, by the end of the 1980s the detergent content in the Odessa Bay and on aquatory of the Odessa port increased 1.5–2 times, compared to the beginning of the decade, and can reach now 2–3 MACs.

5.3.7.4 Phenols

From 1986 to 1989 the mean annual content of these toxic chemicals in Odessa coastal waters increased from 8–10 to 14–16 MACs. By the end of the decade the situation by phenols deteriorated also in the Sevastopol area. However, compared to the data of the 1970s, by the end of this period the mean and maximum phenol concentration in the surface layer of the northwestern Black Sea decreased several times.

5.3.7.5 Organochlorine Pesticides

From 1986 to 1989, the level of water pollution with these toxicants in the open northwestern Black Sea decreased 5–6 times. In 1989, a 3–4-fold decrease in the OCP content was noted also in the Sevastopol Bay and the Dnieper mouth. At the same time, for the last 20 years the OCP concentrations in surface water of the Odessa zone increased 3–4 times.

5.3.7.6 Heavy Metals

At present, because of an irregularity of coastal observations and paucity of data on HM content in water, it is not possible to analyze the dynamics of their pollution level in the area under investigation.

As a result of analyses, the conclusions were made, which may be used for development of recommendations on optimization of water pollution monitoring system on the Black Sea shelf, planning of nature conservation measures, and management of economic activities at its coast:

1. Compared to the beginning of the decade, in the second half of the 1980s the pollutant discharge into the Black Sea with Danube waters reduced: P_{tot}—2 times; N_{tot}—4 times; NH_4^+—5–8 times; oil products and SS—2.5 times; OCP—7 times.
2. For the same time, the supply of such pollutants as NH_4^+, OHC, and SS into the Black Sea with the Dnieper runoff decreased 17, 1.5, and 30 times, respectively, while disposal of P_{tot} increased 2 times.

Nevertheless, in the 1980–1990 the concentrations of such pollutants as OHC, SS, OCP, and phenols in surface water of the northwestern Black Sea exceeded MAC even by mean long-term values. The content of toxic HM exceeded MAC several times but by its maximum values only. During the 1980s an increase in concentrations of P_{tot} and N_{tot} in the Danube offshore zone, oil products off Sevastopol and South Coast of Crimea, pesticides and phenols in the Odessa area was noted. During the same time the tendency to cleaning of Danube offshore waters from oil products and pesticides, and waters of the Danube, Dnieper, and its offshore zone from detergents and pesticides was fixed.

By the beginning of the XXI century these tendencies continued. Moreover, in the near-mouth areas of the Dniester and Dnieper, because of practical suspension of production in the big coastal and watershed cities, during the last decade of the XX century they strengthened essentially that resulted in considerable improvement of water quality in the northwestern Black Sea.

5.3.8 Oil and Chemical Pollution of Bottom Sediments

Not less important than pollution of surface water consequence of economic activities for marine ecosystem is associated with accumulation of polluting substances in bottom sediments. The intensity of this process depends on the content of fine (pelite) fractions and organic matter in grounds, which characterize the type of aquatic geochemical landscape (Fesyunov and Nazarenko 1991; Khovansky and Chernousov 1989). In fine silts, for example, the concentrations of lead and nickel are 5–40 times, titan and vanadium—6–9 times, and copper and manganese—2–8 times higher than in sands. For shell limestone the prevalence of mercury is characteristic that is caused by accumulation of this metal in mollusk valve fragments forming shell limestone (Nazarenko and Ivanova 1988). Moreover, in the near-mouth areas of the Dnieper and Danube the content of copper, lead, nickel, manganese is 1.5–3 times higher than in similar sediments of the Karkinit Bay remote from the river mouths, and the vanadium and zinc concentrations in grounds of the Danube offshore zone are 7 and 11 times higher than in the landscape zones of other areas of the northwestern Black Sea (Fesyunov 1988). In the Danube–Dniester interstream zone the mercury content in bottom sediments is also 2 times higher than in shell limestone of the Karkinit Bay (Nazarenko and Ivanova 1988).

5.3.8.1 Oil Hydrocarbons

According to data of Hydrometeorological Service, the content of oil products in sediments of the most areas of the Black Sea in the 1990s was within MAC. The exceptions were the Odessa coast where their concentrations exceeded the allowable norm 3.5 times (Savin and Podplyotnaya 1991), the Odessa and Karkinit Bays, and the Dnieper offshore zone where their values exceeded MAC by 10–50%. According to data obtained in 1998 (Table 5.2), the content of oil products in bottom deposits of the Danube offshore zone ranges from 30 to 462 mg/kg, Dniester offshore zone—to 216 mg/kg, and Dnieper offshore zone—from 48 to 264 mg/kg that does not exceed the safe level (500 mg/kg).

5.3.8.2 Phenols

The concentrations of this toxic chemical in bottom sediments of the coastal zone of the northwestern Black Sea (Karkinit and Odessa Bays, Dnieper offshore zone) exceed the natural background 3, 9, and 6.5 times, respectively.

5.3.8.3 Organochlorine Pesticides

The maximum OCP concentration in bottom sediments are characteristic of the near-mouth and shallow areas of the coastal zone of the sea, not far from the industrial centers. In mouths of the Southern Bug and Dnieper the OCP content ranges from 94 to 4,800 ng/g. In the areas of Odessa and mouth of Dniester, the OCP content in sediments was 1,024 and 612 ng/g, respectively (Keondzhyan et al. 1990). According to data for 1992–2000, the DDT content in grounds of the northwestern Black Sea can change from 1,600 (center) to 4,100 (Dniester offshore zone) and to 8,300 ng/g (Danube offshore zone) (Orlova and Komorin 2001). In the same zones, the PCB content in bottom sediments amounted to 600, 800, and 1,800 ng/g.

5.3.8.4 Heavy Metals

Mercury

According to data of Institute of Biology of the Southern Seas of the Ukrainian Academy of Sciences (Svetasheva et al. 1990), until 1990 the mercury content in sediments of the northwestern Black Sea changed from 0.02 to 0.29 μg/g of dry weight that by the upper limit exceeded the geochemical background value (GBV) 2–3 times. Such values are characteristic of the Danube offshore sites. According to other authors, the range of fluctuations of this characteristic here can make 0.1–0.5 μg/g of dry weight (Nazarenko and Ivanova 1988) that by the maximum values somewhat exceeds the previous estimations. In 1998 (Table 5.3), in the Danube area the mercury concentrations amounted to 0.035–0.413 μg/g (4 GBVs, in the Dniester area—0.058, and in the Dnieper offshore zone—0.025–0.054 μg/g that corresponds to data for the Danube for 1990.

Copper

In the 1990s, the mean content of this microelement in sediments of the northwestern Black Sea was 21.4 μg/g, and the maxima (70 μg/g) exceeding GBV1.5 times were fixed in zones of silt deposits (Fesyunov 1988). According to the observation data obtained by the HMS network, the copper content on the shoal of the northwestern Black Sea was within the background range. At present, the situation practically did not change—the maximum copper concentration in deposits of the Danube offshore zone can reach 94.4 μg/g (2 GBVs) (Chugai and Safranov 1999).

Lead

In the northwestern Black Sea, at the shelf-averaged values of 15.3 μg/g, the maximum lead concentration in the 1990s were fixed in the Danube area (100 μg/g) that exceeded GBV 5 times (Fesyunov 1988). Today, they are more than 2 times lower here (41.2 μg/g).

Chrome

According to the HMS data, the content of this toxicant in sediments of the northwestern Black Sea ranges from 26 (Karkinit Bay) to 163 (Dnieper offshore zone) μg/g that in the latter case is 2.5 times higher than GBV. The excesses of natural background (1.5–2 times) were fixed also in the zone of silt deposits of the open shelf, in the Danube offshore zone, and in the Odessa Bay. In 1998, in the Danube mouth zone the same concentration (104 μg/g, or 1.5 GBVs) were registered, while in the Dnieper offshore zone they were lower, 99 μg/g.

Zinc

The mean zinc concentration in the northwestern Black Sea is 30.7 μg/g, exceeding the background values 3.7 times. Their maximum values reach here 100 μg/L (Danube offshore) that is 10 times higher than GBV (Fesyunov 1988). According to data for 1998, its content in the Danube offshore zone can reach 84.6 μg/g, in the Dniester area it does not exceed GBV (30 μg/g), and in the Dnieper zone the zinc concentration exceeds GBV 2 times (64.4 μg/g).

The analysis made will allow forth to estimate relatively the contribution of natural gas production on the northwestern shelf to the total level of water and bottom sediment pollution in this area.

5.4 Commercial Hydrobionts and Their Food Objects

The northwestern shelf is the most productive area of the Black Sea. The main stocks of sturgeons, mollusks, seaweed are concentrated here. Moreover, in different seasons this area of the sea is a zone of behavior of the main life cycle stages (spawning, feeding, migrations) for many commercial pelagic fishes and their food objects. By the literary data (Arkhipov 1993), we analyzed a role of the Black Sea area under investigation as a center of life concentration.

5.4.1 Zooplankton

Black Sea zooplankton counts about 120 species of organisms and 20 species of pelagic larvae of bottom invertebrates (Sorokin 1982). The complex of pelagic plankton fauna consists of copepods, cladocerans, chaetognaths, larvaceans, ctenophora, and jellyfishes. The fodder zooplankton includes almost the whole species composition of Black Sea plankton, except for ctenophora, noctiluca, and jellyfishes, which are almost not met in fish stomachs. The share of fodder zooplankton in the raw biomass composition does not exceed 20–27.5%. The other part is represented by organisms with the high water content (ctenophore, noctiluca, jellyfishes).

Depending on the origin, fodder zooplankton is divided into cold-loving species (*Calanus helgolandicus, Pseudocalanus elongatus, Oithona similis*) inhabiting deep layers of the sea, heat-loving species (cladocerans, pantelids, infusorians) disappearing from zooplankton biomass during the cold season, and eurythermic species (*Oithona minuta, Acartia clansi, Paracalanus parvus, O. dioica, S. setosa*) meeting in the sea in all seasons.

In summer, in the Dniester–Danube interstream zone, the occurrence of concentrations of heat-loving forms of fodder zooplankton (concentrations of 50–100 mg/m^3) for the 1985–1989 period reached 70%. In winter, the distribution, scales, and stability of zones of fodder zooplankton concentrations in the Black Sea change essentially. During this season they are displaced from the northwestern Black sea eastward, remaining only in the coastal zone of the Northwest Crimea, from Cape Tarkhankut to Yevpatoria (Fashchuk et al. 1995).

5.4.2 Phytobenthos

The total stock of macrophytes, sea grasses, and periphytic microalgae forming the basis of phytobenthos of the Black Sea reaches 15 million t, and the raw biomass production—50 million t/year. The total biomass of all (more than 380 species) microalgae is only 0.2 million t, and their annual production—15 million t (Fig. 5.9).

From 304 species of macroalgae, 140 species belong to the red, more than 80 species—to the green, and more than 70 species—to the brown algae. From their total number, only 12 species have the commercial importance. 75 species of macrophytes, including all commercial species, are perennial. They have two maxima of development—spring and autumn. In volume, macroalgae grow at depths down to 10–15 m, displacing to 20–25 m near the open coasts with steep slopes. At depths of 40–60 m the Phyllophora population prevails, occupying together with Cystoseira a leading position in marine phytobenthos. Until recently this species was the main commercial object.

In 1909, the "Zernov's Phyllophora Field" occupied almost the whole central part of the northwestern shelf of the sea (Zernov 1909). Its area exceeded 10 thousand km^2, and the seaweed biomass reached 10 million t. In the 1960s, this seaweed community also occupied the area of 11.8 thousand km^2, with the total biomass of 9 million t (Kaminer 1971). But from the beginning of the 1970s the size of this unique biocenosis and Phyllophora stock began to be reduced sharply.

In the late 1970s its total biomass decreased here to 1.4 million t (Katukov 1983), and in the mid-1980s it did not exceed 0.3 million t (Zaitsev 1989), at the field area

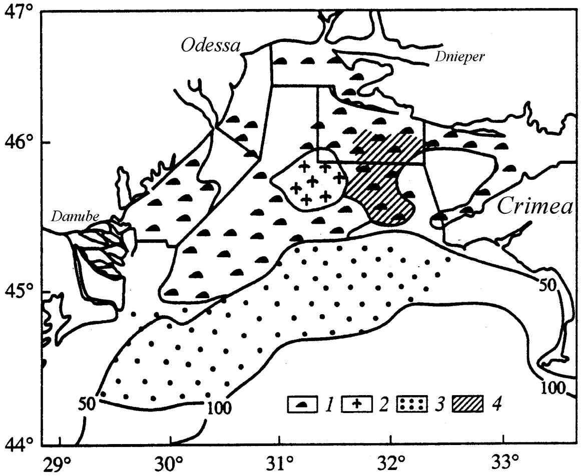


Fig. 5.9 Main biocenoses of the northwestern Black Sea (Samyshev et al. 1986). *1* mussels, *2* Phyllophora nervosa, *3* phaseolina, *4* commercial concentrations of mussels. *Straight lines* correspond to borders of fishery zones

of 4,000 km^2. By the estimations based on the knowledge of Phyllophora photosynthetic activity parameters, until the moment of the degradation beginning, the seaweed community of "Zernov's Phyllophora Field" released up to 2 million m^3 of oxygen into the water during daylight time (Zaitsev 1992). Now, this reserve is lost. At present, the Phyllophora colonies remained only in the coastal zone at depths of 3–5 m, and the insignificant by their area commercial fields of this seaweed are located in the center of the northwestern Black Sea—in the "channel drift" (see Fig. 1.8). Its production here does not exceed several tens of tons per year.

5.4.3 Zoobenthos

From 1,518 species of benthic animals of the Black Sea, mollusks comprise more than 50% of the total biomass and give 90% of the annual production, which reached in the 1960s 23.8 and 50–70 million t, respectively. The stock of fodder zooplankton which includes copepods, polychaetes, oligochaetes, rotifers, amphipods, and other organisms, is 7.7 million t.

Mussel (*Mytilus galloprovincialis*) is bivalve mollusk, which maximum abundance is concentrated in the northwestern Black Sea and the Kerch Strait. Its lifetime is 7–8 years. Mussels mature at age of 2 years. They have two peaks of spawning, in spring and autumn, at temperature from 8 to 13°C. The first 2–4 weeks after shedding, eggs are at the planktonic stage near the sea surface, and then they gravitate to the bottom in the depth range down to 80 m. Mussels reach the commercial size (50 mm) at age of 4–7 years. The individuals at the age of 21–28 years, with length of 110–115 mm are met in the Karkinit and Dzharylgach Bays of the northwestern Black Sea (Project "The Seas …" 1992).

Until the mid-1970s the total area of mussel colonies in the northwestern Black Sea was about 20,000 km^2, and their biomass ranged from 8 to 12 million t. From this moment, the progressing degradation of their population is observed. In the 1980s the total area of mussel banks was reduced to 10,000 km^2, and the total biomass—to 5.6 million t. The fishing stock of mollusks decreased during this period from 2.4 to 0.5 million t (see Fig. 1.8) (Zaitsev 1992).

5.4.4 Pelagic Fishes

5.4.4.1 Black Sea anchovy (*Engraulis encrasicolus ponticus*)

From 165 fish species and subspecies living in the Black Sea, anchovy is one of the most abundant. It has a short life cycle (to 5 years), high reproductive capacity (from 9 to 25 thousand eggs from each female), prefers relatively warm (not lower than 6°C) waters, and is able to spawn in a wide salinity range (from 9–10 to 17–18‰). The mass spawning occurs from May to August, at water temperature of 16–26°C.

In summer, adult individuals of anchovy in 100% of cases are distributed off the Odessa coast and in the central part of the northwestern shelf. In the Dniester–Danube interstream zone the probability of their concentrations decreases to 70%, and in the deepwater shelf sites (the continental slope area over the isobath of 100 m), from Cape Tarkhankut to the Romanian economic zone, it makes 50% of cases (Fashchuk et al. 1995). The probability of occurrence of anchovy eggs in the near-mouth areas of the Dnieper is 100%, and in those of the Dniester and Danube—50–70%. In summer, anchovy juveniles are concentrated steadily in the near-mouth area of the Danube, and in the more seaward shelf areas they are met in 20–30% of cases.

5.4.4.2 Mediterranean Scad (*Trachurus mediterraneus ponticus*)

Until recently, the abundance of this species in the Black Sea ranged from 75 to 800 thousand t. Being heat-loving fish, during the summer period scad lives in the warm surface layer, from 0 to 25–30 m, while in winter, fish is distributed mainly at depths of 30–80 m, and in some cases—at depths from 20 to 120 m. The temperature range in which scad is met more often, is 6–25°C. Scad prefers sea waters and avoids freshened areas, belongs to summer-spawning species; its spawning usually begins at the end of May and lasts until late August, at water temperature of 15–26°C and salinity of 11.6–19.3‰. The optimum temperature for spawning is 19–23°C.

The northwestern shoal (Danube offshore zone) is a traditional area of mature scad concentration (frequency of occurrence is up to 40%). In other parts of the shelf, from the Danube to the Dnieper, mature fish forms the higher concentration only in some years. At early stages of development, scad practically is not met in the northwestern shelf zone.

5.4.4.3 Sprat (*Sprattus sprattus sprattus*)

This species, as well as anchovy, belongs to the most abundant fishes of the Black Sea. In last years, its stock fluctuated from 0.2 to 1.6 million t. Sprat is a winter-spawning species; its spawning period is very long but the mass spawning occurs from October to March in the open sea. Eggs develop within 8 days in pelagial, at temperature of 5–13°C. Fish lives in water layers with mainly low temperature, from 6 to 18°C, avoids the sites with very freshened water, feeds on cold-loving zooplankton species. The sprat lifetime is 5 years.

In March–April, sprat begins to migrate from the open areas of the sea into the coastal zone (mainly, into the northwestern Black Sea), where it turns to the near-bottom habitation. From this period, its wide trawling fishery in the Cape Tarkhankut zone (depths of 50–70 m), northern part of the Danube offshore zone, off the Snake Island (depths of 20–30 m), and on the continental slope of the NWBS along the 100-m isobath, from the Crimean coast to Romania and Bulgaria, begins.

The main centers of mature sprat concentration are located on the northwestern shelf, including the near-mouth areas of the Danube (up to 70% of cases) and Dnieper (to 50% of cases), shelf zone of the 50–100-mile width, from the Romanian coast along the continental slope eastward to Cape Tarkhankut (West Crimea) (up to 50% of cases). On the shallow sites of the northwestern sea sprat eggs are absent, and the frequency of occurrence of its larva and juvenile concentrations does not exceed 10–40%.

5.4.5 Bottom Fishes

5.4.5.1 Sturgeons

Representatives of this bottom fish species live in the coastal zone of the Black Sea practically everywhere but the maximum concentrations, according to YugNIRO data (Project "The Seas …" 1992), are noted in the northwestern Black Sea (see Fig. 1.3). The main spawning and early (3–4 months after spawning) stages of development of Russian sturgeon (*Acipenser guldenstadti*) proceed in the Dnieper (May–July) and Danube (February–September). Sevruga (star sturgeon, *Acipenser stellatus*) spawns in the Danube from March to December, with pauses in July–September, and beluga (*Huso huso*)—from January to June. At the end of May sturgeon juveniles appear in deltas of these rivers. The subsequent feeding until maturation (at age of 8–12 years for sturgeon and sevruga, and 11–14 years for beluga) occurs in the shallow zone of the northwestern sea, while adults are concentrated off the Crimean coast, mainly in the Karkinit Bay (see Fig. 1.4). Today, the abundance of sturgeons in the Black Sea does not exceed today 9 thousand t, and their annual removal as by-catch is 25 t (Domashenko and Akselev 1990). In the 1950s their catch during the regular fishery reached 1,000 t (Photo 5.7).

Photo 5.7 Today fishermen of the Karkinit Bay may only begrudge their American colleagues and recall black caviar as overpast youth [www.latimesblogs.latimes.com]

5.4.5.2 Flounders

Among several representatives of these species living in the sea, Black Sea turbot (*Psetta maeotica*) is the largest, and its population until recently was considered as the most abundant. One of the traditional areas of its habitation, except the Kerch near-strait zone, is the West Coast of Crimea, off Cape Tarkhankut.

Black Sea turbot prefers mainly sandy and muddy bottom and inhabits them to the depths of 100 m. It can reach the size of 1 m, weight of 15 kg, and age of 16 years. Males become mature at age of 4–6 years, and females—at age of 5–7 years. The spawning occurs from March to June at depths of 20–60 m, with water temperature of 8–12°C. Eggs are pelagic, and larvae during the first 2 months after hatching are also distributed in the water column of the coastal zone of the sea. Juvenile fishes migrate into the near-bottom layer, to depths of 2–10 m, in August, where they live 2–3 months. Then, juvenile turbot migrates seaward. In early spring adults (4–7 years) are concentrated for spawning at depths of 30–70 m, in July–August they are displaced to the larger depths, and in October adult turbots approach the coast for feeding (Project "The Seas…" 1992). The fishery on Black Sea turbot was conducted traditionally off the Crimean coast. In the 1960s their annual catch was 2–3 thousand t. Since the mid-1970s its stocks in the northwestern sea began to decrease, and in 1986 the fishery was banned because of almost total disappearance of fish in the zone of the former USSR. From the early 1990s the recovery of turbot population was noted, and in 1994 its experimental-industrial fishery by flounder nets was started in the coastal zone of the Crimea, from Feodosiya to Alushta.

5.4.5.3 Mullets

The main commercial species of mullets, golden mullet (*Liza aurata*) and striped mullet (*Mugil cephalus*), live in the coastal waters practically on the whole sea aquatory, and for most of the year they migrate along the coast. The common size of golden mullet is 12–54 cm. Striped mullet can reach 75 cm and weight of 7 kg. For both species the individuals at age up to 20 years were registered. Mullets become mature at age of 3–4 years. The spawning occurs only in the coastal zone of the sea from May to August. Fecundity of golden mullet ranges from 0.8 to 3, and that of striped mullet—from 1 to 12 million eggs. Pelagic eggs are transported by currents for distance of 50–100 miles from the coast.

In June–July, juvenile mullets approach the coast, enter limans and river mouths for feeding, but their main feeding grounds are located in the Karkinit Bay of the northwestern Black Sea and in the Sea of Azov. Wintering of fish and spring trophic migrations occur outside the northwestern shelf. By the end of the 1960s, the annual mullet catch, amounted to 20–40 thousand t in the pre-war period, was reduced 10 times and did not exceed 0.2–0.4 thousand t. Now, the fishery on these mullet species is almost ceased because of reduction in abundance of their populations.

The analysis made will enable in future to estimate operatively, what hydrobionts species, in what season, and in what condition can be impacted by polluting substances containing in water and bottom deposits.

5.5 Environmental Monitoring in the Gas Production Areas in the Karkinit Bay of the Black Sea

To control the impact of this type of economic activities on the ecosystem of the northwestern shelf of the Black Sea, the complex hydrogeochemical monitoring of environmental conditions in the areas of drilling operations and commercial gas production was established since 1986 (Fashchuk et al. 2006a, b).

Its objectives included the assessment of the current oceanographic conditions that control the formation of pollution fields in the zones of development of offshore gas fields in the Karkinit Bay of the Black Sea, study of spatiotemporal variability of environment pollution level in the area of offshore gas production (Karkinit Bay), and identification of possible mechanisms of this process.

To assess marine environment pollution in the operation zone of SSP, the data of 12 site surveys (1987–1993), with measurements of OP, Hg, Cu, Pb, Cd, Cr in the Karkinit Bay, included from 7 to 12 stations spaced 10–20 miles apart, were used (Fig. 5.10).

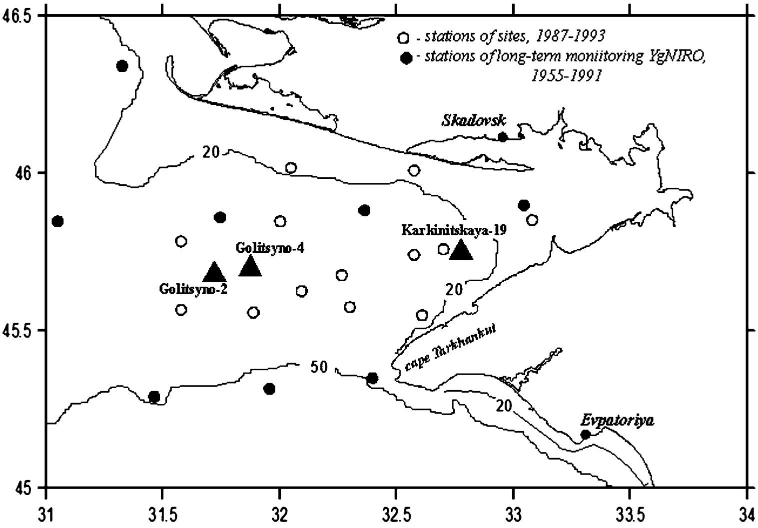


Fig. 5.10 Scheme of stations of monitoring conducted by YugNIRO (1987–1993) and location of operating stationary sea platforms (SSP) in the Karkinit Bay of the Black Sea (Fashchuk et al. 2006a)

In 1991 and 1993, the observations in this testing area were made over a denser (50 stations) network. During this time, about 2,500 determinations of microelements (Hg, Cu, Pb, Cd, Cr), total oil products (OP) in water (300–400 determinations of each component), and about 1,500 determinations of the same toxicants in bottom sediments were made on the NWSH of the sea. The methods and equipment used for water sampling and hydrochemical determinations are described in Petrenko et al. (2002).

5.5.1 Interannual Dynamics of Marine Environment Pollution in the Zone of Gas Field Production

The observations on pollution of water and bottom sediments in the Karkinit Bay were launched in 1975 by organizations of former Goskomgidromet of the USSR. The results of their treatment were published in the State Water Cadastre, Bulletins on the State of Chemical Pollution of the Black and Azov Seas, and in Yearbooks of Hydrochemical Data on Sea Water Quality (Table 5.4).

Before 1977, the mean total OP content in the surface and near-bottom water layers exceeded MAC steadily 10–20 times. Their maximum concentrations (2,900 μg/L, or 58 MACs) were fixed in 1977. By 1984, the pollution of bay waters with OP somewhat decreased, but the mean and maximum concentrations of OP were still 2.5–4 and 4–6 times higher than the respective norms. This suggested that, after the introduction of more rigorous measures on the control of OP transportation in the early 1978–1982, the rather strong sources of marine environment pollution still persisted in the area. These sources, most probably, were associated with oil spills during its transportation and marine production of hydrocarbons.

Indeed, the analysis of data obtained by aircraft monitoring of OP films on the aquatory of the Black and Azov Seas in 1981–1990 showed that the annual frequency of occurrence of the zones of their accumulation on the NWSH of the Black Sea (Danube–Odessa area) decreased in this period from 70–100 to 30–50% of cases. Nevertheless, according to these data, during the monitoring period oil slicks with the area of 30–220 km^2 were registered on the Karkinit Bay aquatory (Photo 5.8).

Table 5.4 Mean/maximum concentrations of oil products (OP) in water, μg/L, and bottom sediments, μg/g of dry weight, in the Karkinit Bay in 1975–1984

Medium	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984
Water (0 m)	$\frac{1.0}{1.9}$	$\frac{490}{2660}$	$\frac{7.7}{19.9}$	$\frac{400}{1040}$	$\frac{0.08}{0.21}$	$\frac{0.9}{1.5}$	–	$\frac{98}{125}$	$\frac{0.14}{0.70}$	–
Sediments	$\frac{16.1}{40.9}$	$\frac{50.2}{171.7}$	–	$\frac{0.41}{2.50}$	$\frac{16.4}{65.7}$	$\frac{235}{478}$	–	–	–	$\frac{0.04}{0.08}$

dash means no data available

Photo 5.8 Oil films (*top* [www.lh6.ggpht.com]) prevent the penetration of solar heat end oxygen into the water column (*bottom* [www.img-fotki.yandex.ru])

5.5.1.1 Oil Products

Water

The first signs of exceedance of total OP content in waters of the NWSH of the Black Sea over the MAC were detected by the authors during the surveys conducted in August, 1988 (1.5 times) and February, 1989 (2.5 times) (Table 5.5, Fig. 5.11a, b). These anomalies were registered in the near-bottom water layer and displayed themselves only maximum concentration values. Beginning from April, 1989 and up to the end of the monitoring period (September, 1993), the OP pollution of shelf water always exceeded the MAC in the whole water column in terms of both the mean (up to 2 MACs) and maximum (up to 14 MACs) values of total OP content. These characteristics reached their maximum in the zone around the *Karkinitskaya*-19 SSP (radius of 6.6 cables—1.5 km) a month after the beginning of exploratory drilling here (30–31 July, 1989).

The values in the surface layer amounted to 544 (11 MACs) and 1,337 μg/L (26.5 MACs), respectively, whereas those in the near-bottom layer were 859 for

Table 5.5 Mean/maximum concentrations of microelements and OP in water, μg/L, and bottom sediments, μg/g of dry weight, on the NWSH of the Black Sea for 1987–1993

Date	Number of stations and determinations: water/sediments	Medium	Hg	Cu	Pb	Cd	Cr	OP
June, 08–12 1987	9 on 35/9	Water (0 m)	$\frac{0.036}{0.070}$	$\frac{0.85}{1.78}$	–	$\frac{0.42}{0.50}$	–	$\frac{28}{75}$
		Water (at the bed)	$\frac{0.013}{0.030}$	$\frac{0.80}{2.09}$	–	$\frac{0.47}{0.74}$	–	$\frac{21}{45}$
		Sediments	$\frac{0.055}{0.090}$	$\frac{9}{25}$	–	$\frac{0.7}{0.9}$	–	$\frac{7}{38}$
September 07–12, 1987	9 on 35/9	Water (0 m)	$\frac{0.025}{0.060}$	$\frac{3.25}{14.85}$	–	$\frac{0.36}{0.61}$	–	$\frac{14}{18}$
		Water (at the bed)	$\frac{0.015}{0.040}$	$\frac{1.35}{2.54}$	–	$\frac{0.36}{0.77}$	–	$\frac{14}{27}$
		Sediments	$\frac{0.067}{0.14}$	$\frac{12.4}{39.7}$	–	$\frac{0.43}{0.54}$	–	$\frac{3.3}{13.6}$
November 24–25, 1987	9 on 22/9	Water (0 m)	–	$\frac{1.42}{3.40}$	–	$\frac{0.35}{0.55}$	–	$\frac{17}{90}$
		Water (at the bed)	–	$\frac{1.40}{3.59}$	–	$\frac{0.41}{0.63}$	–	$\frac{26}{44}$
		Sediments	–	$\frac{10.5}{35.4}$	–	$\frac{1.9}{2.8}$	–	$\frac{150}{270}$
August 17–19, 1988	9 on 33/9	Water (0 m)	$\frac{0.026}{0.055}$	$\frac{0.80}{1.79}$	–	$\frac{0.19}{0.29}$	–	$\frac{19}{25}$
		Water (at the bed)	$\frac{0.009}{0.019}$	$\frac{1.92}{4.10}$	–	$\frac{0.24}{0.41}$	–	$\frac{35}{81}$
		Sediments	$\frac{0.1}{0.2}$	$\frac{11.0}{25.6}$	–	$\frac{1.3}{2.6}$	–	$\frac{1120}{3640}$
February 1989	10 on 20/10	Water (0 m)	$\frac{0.184}{0.360}$	$\frac{2.125}{4.115}$	$\frac{0.253}{0.890}$	$\frac{0.218}{0.503}$	$\frac{0.998}{1.337}$	$\frac{16}{139}$
		Water (at the bed)	$\frac{0.133}{0.220}$	$\frac{1.880}{3.698}$	$\frac{0.292}{0.787}$	$\frac{0.274}{0.484}$	$\frac{1.401}{1.681}$	$\frac{29}{89}$
		Sediments	$\frac{0.06}{0.19}$	$\frac{3.434}{5.522}$	$\frac{0.416}{0.600}$	$\frac{0.171}{0.290}$	$\frac{2.226}{2.761}$	$\frac{159}{340}$
April, 1989	7 on 14/7	Water (0 m)	$\frac{0.466}{0.480}$	$\frac{1.097}{2.224}$	$\frac{0.031}{0.088}$	$\frac{0.539}{1.375}$	$\frac{0.964}{2.185}$	$\frac{80}{133}$
		Water (at the bed)	$\frac{0.458}{0.600}$	$\frac{0.940}{2.272}$	$\frac{0.028}{0.047}$	$\frac{0.637}{0.760}$	$\frac{0.793}{0.898}$	$\frac{75}{125}$
		Sediments	$\frac{0.074}{0.104}$	$\frac{3.509}{5.825}$	$\frac{1.759}{2.703}$	$\frac{0.002}{0.008}$	$\frac{3.354}{4.382}$	$\frac{89}{173}$
July, 30–31 1989	12 on 24/12	Water (0 m)	$\frac{0.437}{0.680}$	$\frac{1.432}{2.980}$	$\frac{0.249}{0.560}$	$\frac{0.274}{0.500}$	$\frac{1.445}{3.240}$	$\frac{544}{1337}$
		Water (at the bed)	$\frac{0.513}{0.690}$	$\frac{1.803}{3.110}$	$\frac{0.303}{0.570}$	$\frac{0.271}{0.580}$	$\frac{1.774}{4.380}$	$\frac{859}{2099}$
		Sediments	$\frac{0.088}{0.207}$	$\frac{2.707}{4.555}$	$\frac{3.792}{4.872}$	$\frac{0.561}{0.778}$	$\frac{12.362}{17.285}$	$\frac{207}{376}$
March 20–27, 1990	25 on 50/25	Water (0 m)	$\frac{0.09}{0.14}$	$\frac{1.970}{4.104}$	$\frac{0.149}{0.322}$	$\frac{0.066}{0.096}$	$\frac{1.289}{2.282}$	$\frac{90}{676}$
		Water (at the bed)	$\frac{0.09}{0.17}$	$\frac{4.348}{19.555}$	$\frac{0.580}{3.739}$	$\frac{0.059}{0.084}$	$\frac{4.464}{27.799}$	$\frac{112}{715}$
		Sediments	$\frac{0.05}{0.16}$	$\frac{10.350}{17.129}$	$\frac{4.038}{5.164}$	$\frac{0.190}{0.306}$	$\frac{10.383}{15.505}$	$\frac{474}{1166}$
August 10–13, 1990	25 on 50/25	Water (0 m)	$\frac{0.21}{0.27}$	$\frac{1.591}{2.654}$	$\frac{0.758}{3.525}$	$\frac{0.199}{0.615}$	$\frac{1.177}{1.837}$	$\frac{85}{313}$
		Water (at the bed)	$\frac{0.18}{0.23}$	$\frac{1.489}{2.079}$	$\frac{0.149}{0.427}$	$\frac{0.051}{0.536}$	$\frac{1.339}{1.915}$	$\frac{100}{182}$
		Sediments	$\frac{0.08}{0.10}$	$\frac{14.356}{24.591}$	$\frac{6.893}{37.207}$	$\frac{0.293}{0.366}$	$\frac{14.600}{21.638}$	$\frac{707}{1533}$
July 09–15, 1991	31 on 50/31	Water (0 m)	$\frac{0.22}{0.71}$	$\frac{2.6}{7.4}$	$\frac{1.368}{3.9}$	$\frac{0.05}{0.32}$	$\frac{1.632}{3.6}$	$\frac{54}{173}$
		Water (at the bed)	$\frac{0.20}{0.79}$	$\frac{2.0}{5.8}$	$\frac{1.817}{11.0}$	$\frac{0.12}{1.45}$	$\frac{1.526}{3.7}$	$\frac{95}{110}$
		Sediments	$\frac{0.02}{0.05}$	$\frac{19.79}{29.00}$	$\frac{22.61}{43.20}$	$\frac{0.10}{0.28}$	$\frac{14.24}{24.9}$	$\frac{534}{1429}$

(continued)

Table 5.5 (continued)

Date	Number of stations and determinations: water/sediments	Medium	Hg	Cu	Pb	Cd	Cr	OP
August, 1992	8 on 16/8	Water (0 m)	–	–	–	–	–	–
		Water (at the bed)	$\frac{0.23}{0.39}$	$\frac{1.0}{1.9}$	$\frac{7.7}{19.9}$	$\frac{0.08}{0.21}$	$\frac{0.9}{1.5}$	$\frac{98}{125}$
		Sediments	$\frac{0.14}{0.70}$	$\frac{16.1}{40.9}$	$\frac{50.2}{171.7}$	$\frac{0.41}{2.50}$	$\frac{16.4}{65.7}$	$\frac{235}{478}$
September 20–23, 1993	53 on 22/49	Water (0 m)	–	–	–	–	–	–
		Water (at the bed)	$\frac{0.04}{0.08}$	$\frac{0.71}{2.36}$	$\frac{2.03}{7.95}$	$\frac{0.09}{0.62}$	$\frac{1.15}{2.11}$	$\frac{100}{181}$
		Sediments	$\frac{0.15}{0.60}$	$\frac{7.88}{19.66}$	$\frac{15.30}{179.5}$	$\frac{0.17}{0.83}$	$\frac{12.60}{42.21}$	$\frac{1730}{11020}$
MAC for water			0.1	5	10	10	1	50
GBV for sediments			0.4	40	20	0.3	84	1000

mean and 2,099 μg/L for maximum values, or 17 and 42 MACs, respectively. The extremely high total OP concentrations at the surface and near the bottom, 5,504 and 13,251 μg/L, or 110 and 265 MACs, respectively, were noted in this time in the immediate vicinity of the *Karkinitskaya*-19 SSP.

Bottom Sediments

In August 1988, the maximum total content of OP in bottom sediments of the NWSH of the Black Sea for the first time exceeded (3.5 times) the geochemical background (GBV), equal to 1,000 μg/g of dry weight. Since March, 1990 these anomalies became stable. First, they displayed themselves in the maximum values of total OP concentrations (up to 1.5 GBVs), and since September, 1993 they could be seen in the mean values (up to 1.7 GBVs). Only in 1992, the OP content in bottom sediments of the area was within the norm but in the next year the pollution increased again sharply. On September 20–23, 1993 the extremely high concentrations of total OP in sediments (11,020 μg/g of dry weight, or 11 GBVs) were observed at the plugged and abandoned *Shmidta*-6 SSP (Table 5.5, Fig. 5.11c).

5.5.1.2 Microelements

Water

Concentrations of dissolved forms of Cu, Pb and Cd in water of the NWSH of the sea throughout the whole monitoring period almost did not exceed the MAC, except for Cu, the content of which after 1990 in some cases was 1.1–1.5 time higher than the norm, and sometimes (March, 1990) 4 times higher (Table 5.5, Fig. 5.11a, b).

The most significant deviations from the norm during the monitoring period were noted for Hg and Cr. The Hg concentrations in water began to exceed the MAC (by a factor of 2–5 for mean values and 5–7 for maximum values) first in the

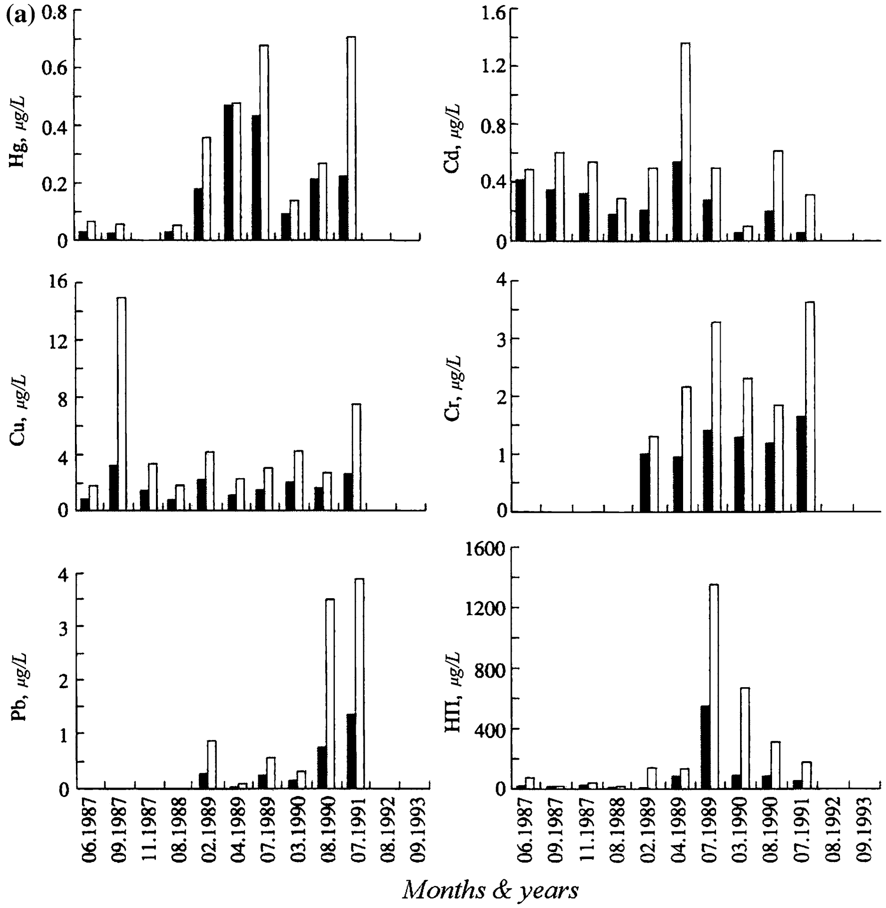


Fig. 5.11 Dynamics of toxicant concentrations in the Karkinit Bay in the period of hydrogeochemical monitoring, 1987–1993. **a** Water (surface), **b** water (near-bottom layer), **c** bottom sediments

surface (February, 1989), and then and in the near-bottom (April, 1989) layers. From this moment and until September, 1993 such anomalies were recorded permanently, and their maximum was reached in July, 1989 in terms of both mean values (up to 0.513 μg/L) and maximum values (up to 0.790 μg/L).

Within almost the whole observation period the mean content of Cr in the surface layer of shelf water was within the MAC (up to 1 μg/L) or exceeded it 1.2–1.5 times. However, the maximum values reached 2–3 MACs. In the near-bottom layer the water pollution with Cr was even higher. Anomalies of mean and maximum concentrations reached here 1.7 and 4.4 MACs, respectively (Table 5.5). The extreme level of shelf water pollution by this toxicant was fixed in the near-bottom layer in March, 1990, when it amounted to 4.464 μg/L in terms of mean values and 27.799 μg/L in terms of maximum values, or 4.5 and 28 MACs, respectively.

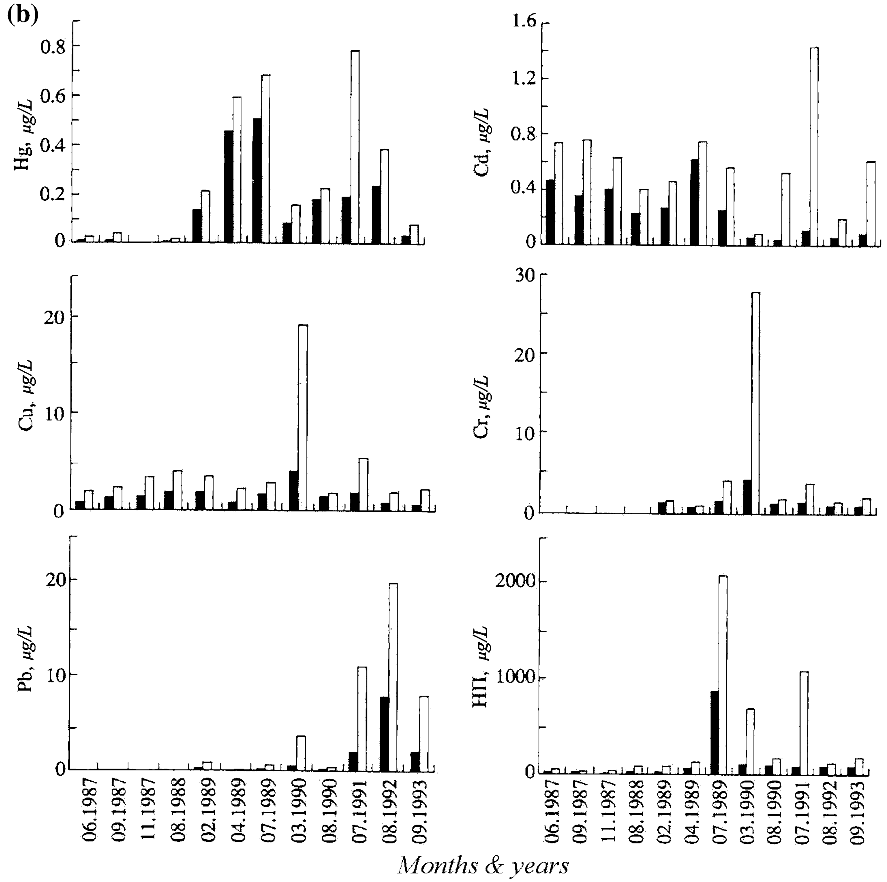


Fig. 5.11 (continued)

Bottom Sediments

In 1987–1993, no cases of anomalous pollution of bottom sediments on the NWSH of the Black Sea with Cr were fixed (Table 5.5, Fig. 5.11c). Among all toxicants, the Cd concentration was the first (July, 1989) to exceed the GBV (0.778 µg/g of dry weight, or 2.5 GBVs), then (since July, 1990) the Pb concentrations exceeded the respective GBV (37.21 µg/g of dry weight, or about 2 GBVs), and after that (since August, 1992), Hg (0.7 µg/g of dry weight, or 1.8 GBVs) and Cu (40.9 µg/g of dry weight, or 1.1 GBVs) concentrations exceeded such levels. The extreme pollution of bottom sediments by microelements for the whole monitoring period was registered in August, 1992 and September, 1993. Concentrations of Hg in this case amounted to 0.6–0.7 µg/g (1.5–1.8 GBVs), Pb, to 180 µg/g (9 GBVs), and Cd, to 2.5 µg/g (8 GBVs).

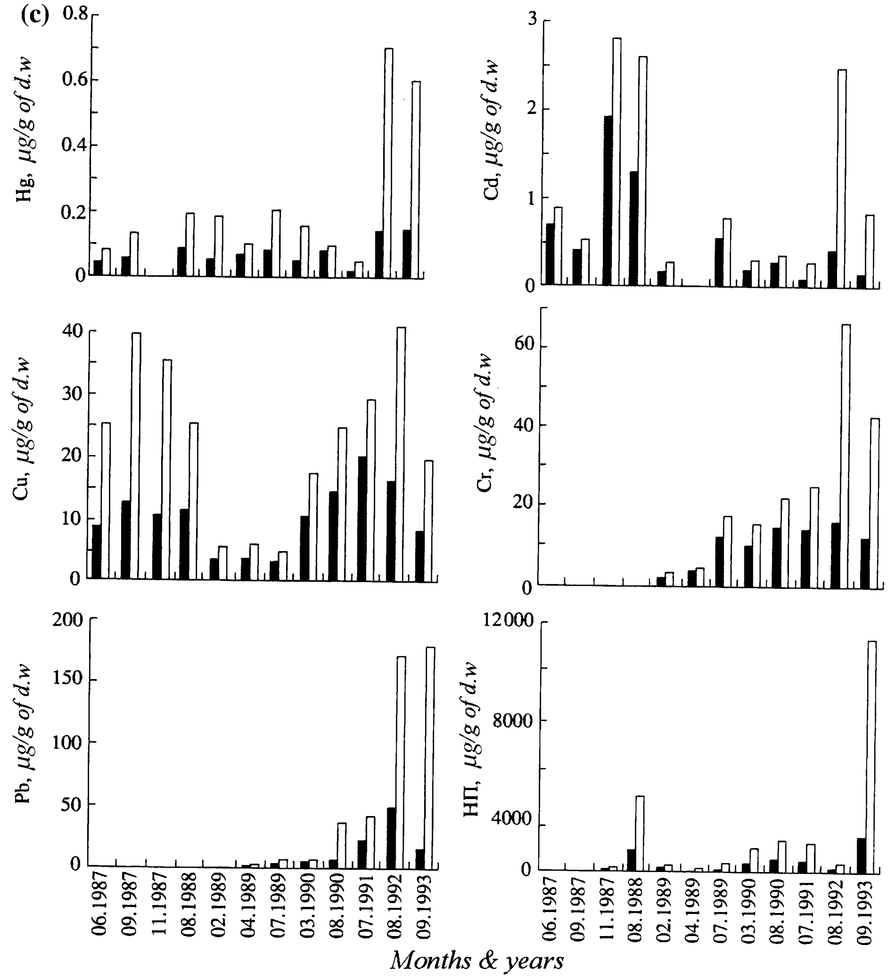


Fig. 5.11 (continued)

5.5.2 Spatial Variability of Oil and Chemical Pollution of Marine Environment

5.5.2.1 Oil Products

Water

The first signs of the new period of increased water pollution with OP in the Karkint Bay (after a relative improvement of situation in 1980–1984) were recorded in November, 1987 (90 μg/L, or 1.8 MACs) and August, 1988 (81 μg/l, or 1.6 MACs) off its northern coast and in the operation zone of *Golitsyno*-4,5 SSP in the open part of the sea adjacent to the bay. At this time, the concentration of OP in bottom sediments increased here almost tenfold as compared with 1987.

In February 1989, the character of OP distribution in the bay waters remained the same. The maximum concentration were also observed in the *Golitsyno*-4,5 SSP zone and northern bay, but they were higher than in previous year (2.1–2.8 MACs). In April 1989, after the construction of the *Karkinitskaya*-19 SSP was competed, the maxima of water pollution with OP (1.6–2.7 MACs) were still observed in zone B, but as early as a month after the beginning of exploratory drilling (August, 1989), the OP concentration on the Karkinit Bay aquatory around SSP (radius of 6.6 cables) exceeded the MAC 5–265 times.

By March-August 1990, the average pollution of water column in the bay with OP decreased to 2 MACs. Only in the near-bottom layer in the zones of operating SSPs it exceeded the norm 13–14 times by the maximum values. Here (new *Karkinitskaya*-19 SSP) mean OP concentrations in sediments were found to increase (up to 474–707 μg/g of dry weight but not higher than GBV) more than twice as compared with 1989. At the same time, the maximum OP concentration in sediments (1,166–1,533 μg/g of dry weight) near the *Golitsyno*-4,5 SSP, which has been operated for 6 years by this time, exceeded the GBV by a factor of 1.5, and circumjacent background value, by a factor of 4.5.

In August 1991, three zones could be identified in the Karkinit Bay in terms of OP concentration in surface water: the western zone, with the operating *Golitsyno*-4,5 and *Schmidta*-6 SSPs (since 1984), and *Golitsyno*-2,18 SSP (since 1990); the southern zone, with the exploratory *Arkhangelskaya*-7, *Shhtormovaya*-17 SSPs, and projected *Shtilevaya-1* SSP; and the eastern zone within the bay, where the *Karkinitskaya-19* SSP started the commercial gas production in 1990 (Fig. 5.12a).

The maximum concentration of total OP (280 μg/L, or 5.5 MACs) was fixed in the western zone at the base of the operating *Golitsyno-2* platform. In the southern zone of exploratory drilling, the OP content in water did not exceed the MAC; in the Karkinit Bay, near the *Karkinitskaya*-19 SSP, which had been put into operation not long before, as well as in the northern part of the bay, the OP concentrations reached 3 MACs (140 μg/L). Near *Schmidta*-6 SSP, which was plugged and abandoned in 1990, the value of this characteristic in 1991 did not exceed the MAC (50 μg/L) and decreased almost tenfold as compared with 1990.

In 1991, the maximum pollution of the near-bottom water layer (up to 600 μg/L, or 12 MACs) was also fixed in local areas in the zone of operating drilling platforms in the western and northwestern part of the aquatory (map is not shown). The near-bottom water pollution in the adjacent southern and eastern aquatories was almost within the norm (50–80 and 10–40 μg/L, respectively).

Bottom Sediments

A zone of maximum values can be identified on the map of total OP concentrations in the surface layer of bottom sediments in July, 1991 (Fig. 5.12b); this zone is

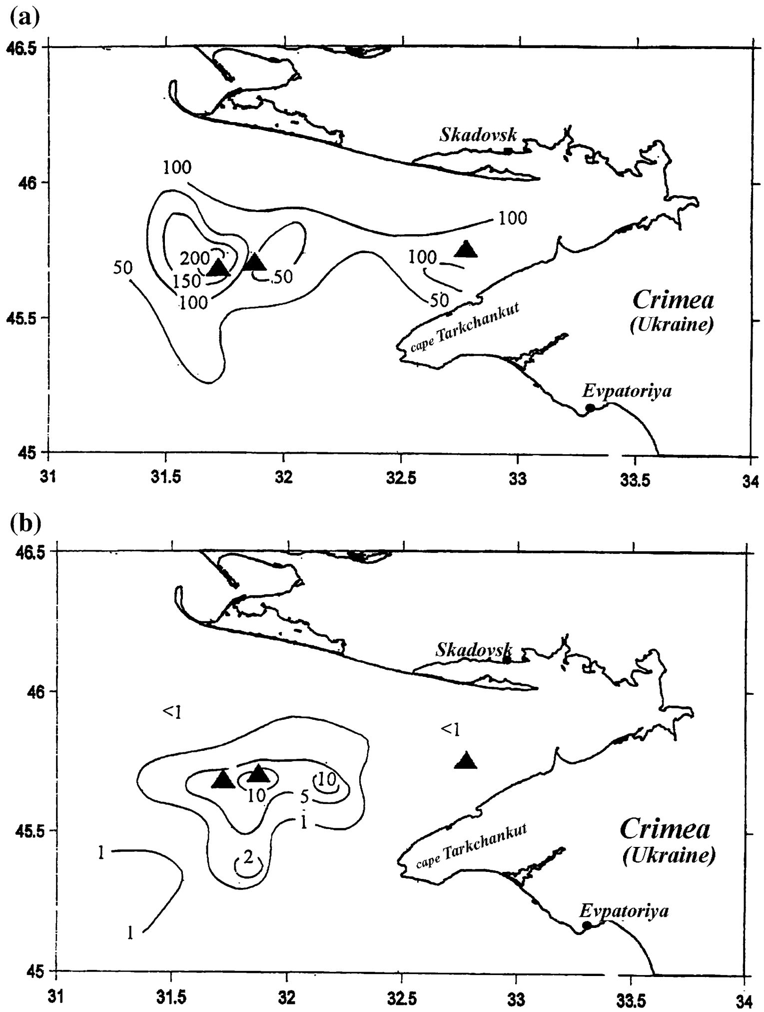


Fig. 5.12 Distribution of total concentrations of OP in **a** the surface water layer, μg/L, and **b** bottom sediments, thousands of μg/g of dry weight, (**b**) in the Karkinit Bay in July 1991

associated with the operating drilling platforms: *Golitsyno*-18 (6,142 μg/g), *Golitsyno*-2 (3,519 μg/g), *Golitsyno*-4 (13,886 μg/g), *Golitsyno*-5 (1,130 μg/g), and *Schmidta*-6 SSP (10,380 μg/g), which was plugged and abandoned in 1990. These values exceed the established current GBV (1,000 μg/g) 6, 3.5, 13.9, 1.1, and 10.4 times, respectively.

At the southernmost exploratory *Shtormovaya-17* SSP, which, as the operating drilling platforms, subject to intensive advection of OP from the central part of the NWSH of the Black Sea, and from the South Coast of Crimea, the OP content in sediments at the wells amounted to 2,200 μg/g (2 GBVs), and at the exploratory

Arkhangelskaya-7 SSP it coincided with the high background level for the entire aquatory of the NWSH of the sea (from 100 to 1,430 μg/g).

In 1991, the lowest OP concentrations in sediments were observed in the inner part of the Karkinit Bay near the drilling *Karkinitskaya*-19 *SSP*, which had been in operation for only one year and was remote from the additional sources of OP. The concentration of OP in sediments here did not exceed 460 μg/g (Fig. 5.12b).

In 1993, the character of the distribution of water column pollution with OP remained unchanged. Their concentrations in the near-bottom layer at the base of SSP were 2–3.5 times above the MAC. The pattern of the distribution of bottom sediment pollution with OP has not changed also. Its maxima were fixed at the bases of the operating *Golitsyno*-4, 5, *and* 18 SSPs (1,360, 1,710, and 2,640 μg/g, or 1.4, 1.7, and 2.6 GBVs). With that, at the *Golitsyno*-4, 18 SSPs the concentrations of OP in sediments decreased 10 and 2.5 times as compared with 1991, while at the *Golitsyno*-5 SSP they increased by a factor of 1.5.

The total OP content in bottom sediments at the exploratory *Arkhangelskaya*-7 and *Shtormovaya*-17 SSPs (920–2,500 μg/g) in 1993 also exceeded the background values and GBV but the situation at the *Schmidta*-6 well (11,020 μg/g, or 11 GBVs) plugged and abandoned in 1990, in this year, as in previous years, remained extreme for the area.

5.5.2.2 Microelements

Water (0 m)

The characteristic feature of spatial distribution of all heavy metals investigated under the monitoring, in the surface water layer is association of their concentration maxima with the bases of drilling platforms (Fig. 5.13, left). This effect is especially strong in case of Hg (up to 3.5–4.4 MACs) at the *Golitsyno*-2 and *Shmidta*-6 SSPs; Cu (up to 2 MACs) at the *Golitsyno*-5 and *Arkhangelskaya*-7 SSPs; Pb and Cd (< MAC) at the SSP of the Golitsyn Elevation; and Cr (from 2.2 to 5 MACs) at all SSPs.

In addition to this spatial pattern of Hg in surface water of the Karkinit Bay, this element is characterized also by an increase in concentration above the MAC in the northwestern part of the bay at the boundary with the centre of the NWSH, and in the southern part of the bay at the boundary with the open sea. An increase in the Cu concentration in the surface layer was also observed not only in the zones of SSPs but in the northern coastal zone of the Karkinit Bay.

Water (Bottom)

For distribution of most microelements (Cu, Pb, Cd, Cr) in the near-bottom water layer the association of their concentration maxima with the bases of wells in operation remains the characteristic feature. The only exception is the

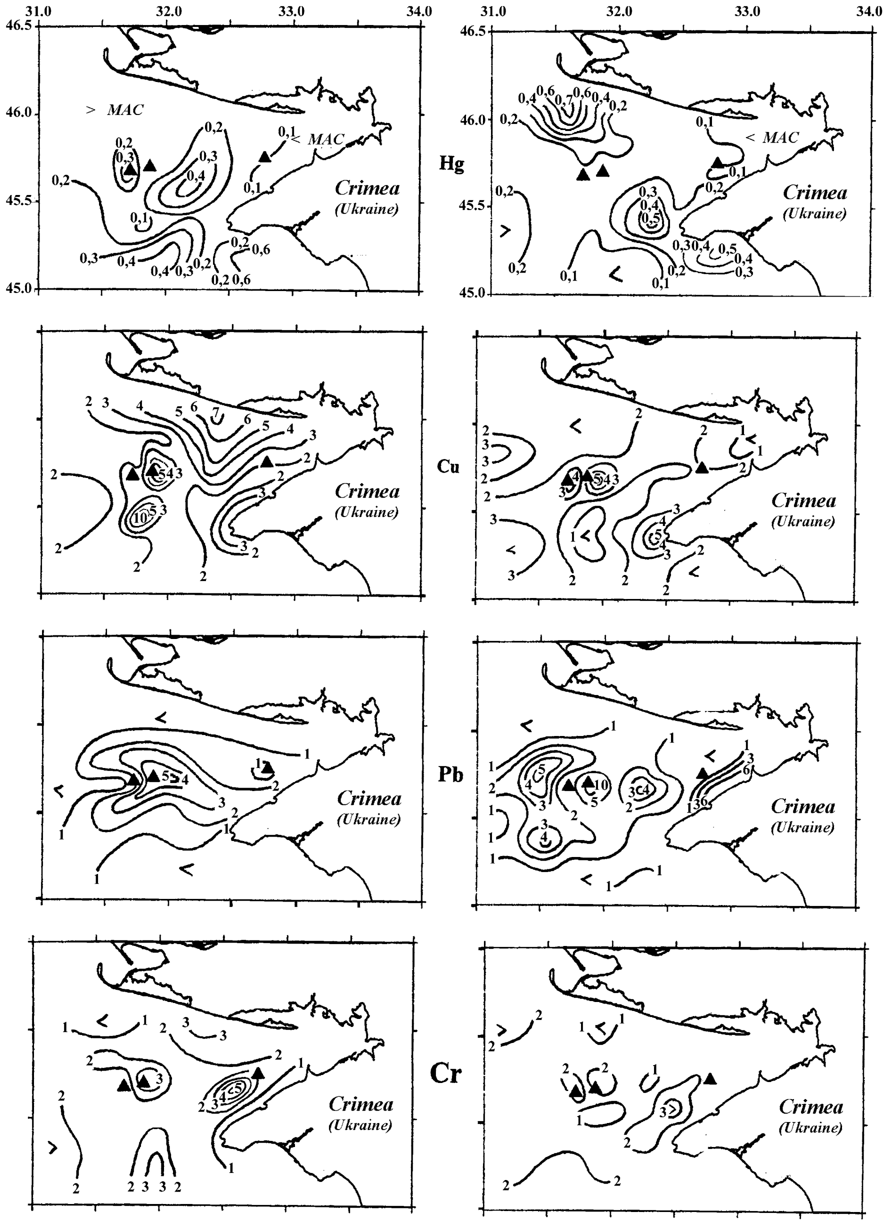


Fig. 5.13 Distribution of microelements, µg/L, in the surface (*left*) and near-bottom (*right*) water layers of the Karkinit Bay in July 1991

Karkinitskaya-19 SSP located in the inner part of the Karkinit Bay (Fig. 5.13, right). The maxima of Cu, Pb, and Cr concentrations were fixed there to the south and southeast of SSPs, off the coast of Cape Tarkhankut. Moreover, unlike other elements, the distribution of Hg in the near-bottom water does not show any association with the position of drilling platforms. Its maxima, on the contrary, are located beyond the SSP zones in the north (in the coastal zone) and in the southeastern part of the area (Cape Tarkhankut) adjoining the open sea.

Bottom Sediments

The distribution of microelements in the surface layer of bottom sediments in 1991 and 1993 was characterized by maxima at the bases of wells of the operating drilling platforms. Such localization of maxima of sediment pollution in 1993 was less distinct than in 1991. Moreover, the distribution of Cr concentration in sediments of the Karkinit Bay in 1993 (Fig. 5.14b), unlike 1991 (Fig. 5.14a), did not show any association with the position of SSPs.

The concentrations of Hg, Cu, and Cr in sediments near SSPs did not exceed the GBV limits. However, the concentrations of Pb exceeded the natural background level 16.5–50 times (from 336.8 to 1,018.2 μg/g) and those of Cd (1.09–3.18 μg/g) were 1.1–10 times higher than the respective background value. The concentration of microelements in sediments decreased 10–100 times at the distance of 1 cable from wells.

5.5.3 Comparison of Monitoring Results with Characteristics of Pollution in Other Regions of the World Ocean

5.5.3.1 Water

Oil Products

The comparison of the obtained estimates of oil pollution of the northwestern Black Sea shelf with the results of similar studies in other parts of the reservoir (see Sects. 5.3.5, 5.3.8) shows that in 1987–1993, the water pollution with OP in the zone of gas fields (Karkinit Bay) even in the extreme cases (14–26 MACs) was, nevertheless, lower than in previous years off the Odessa and Sevastopol coasts, but it was much greater than that observed in the late 1990s on the rest of the northwestern Black Sea shelf. It does not contradict the data of other authors (Pankratova et al. 1993; Semenov and Pavlenko 1991). In extreme situations, water pollution with OP on the NWSH of the sea was 3–6 times higher than in the Indian and Pacific oceans, but it almost coincided with pollution of Atlantic waters on tanker routes and in the areas of offshore oil and gas production (the North and Norwegian seas). Such conclusions do not refer to the case of extremely high OP concentrations (up to 265 MACs) near the base of the *Karkinitskaya*-19 SSP one month after the beginning of exploratory drilling (August, 1989).

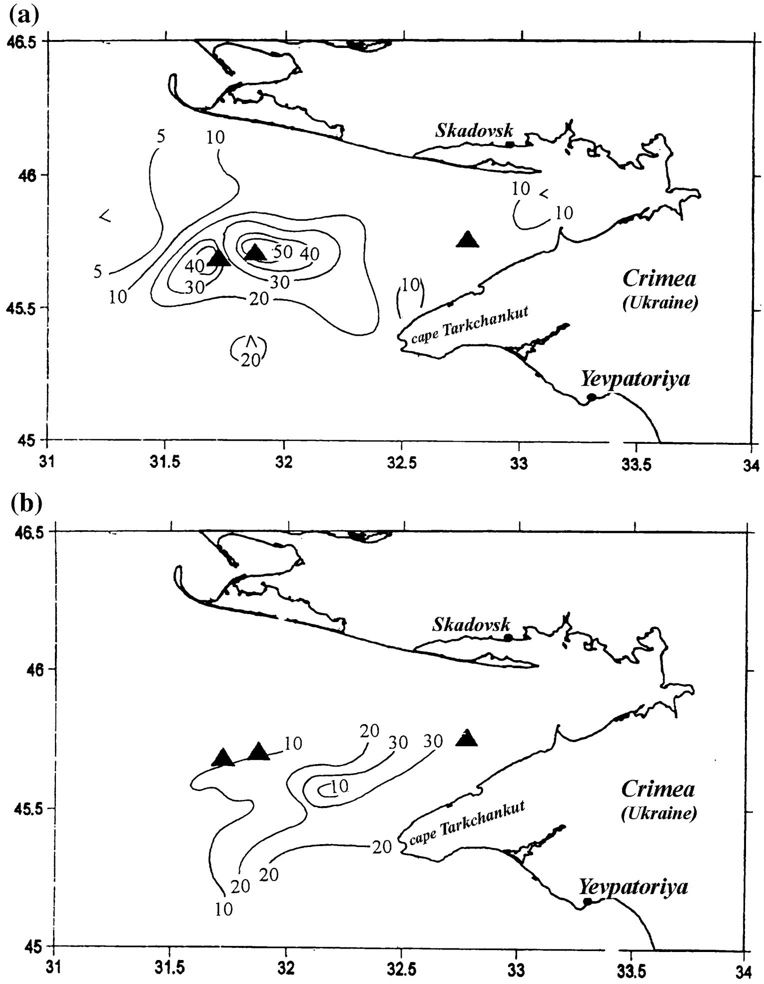


Fig. 5.14 Distribution of Cr, µg/g of dry weight, in July 1991 (**a**) and September 1993 (**b**) in bottom sediments of the Karkinit Bay

Microelements

During the monitoring period (1987–1993) the maximum (5–7 MACs) water concentrations of Hg in zones of SSP location corresponded to the level of water pollution with this toxicant in the offshore zone of the Dnieper-Bug Liman and near-Bosporus area, were 2–3 times higher than those in the near-mouth areas of the Dnieper and Danube, and 2–3 orders (!) of magnitude greater than its concentrations in the zones of oil hydrocarbon production in the Gulf of Mexico and the North Sea.

In extreme cases, mean Cr concentrations in water of the area under investigation (4.5 MACs) were twice as large as those measured in waters of Georgia (2.7 MACs) but coincided with the values characteristic of ground dumping zones on the NWSH of the sea and along the North Caucasian coast (up to 6 MACs). The maximum water concentrations of Cr (28 MACs) on the northwestern shelf in 1987–1993 exceeded the values for other parts of the Black Sea 4–5 times and those for the Gulf of Mexico and the North Sea, 10–50 times.

5.5.3.2 Bottom Sediments

Oil Products

Concentrations of OP in sediments at the well bases during the exploratory drilling on the northeastern Sakhalin shelf did not exceed 8–30 μg/g. However, during the long-term commercial development of fields, in case of use of oil-containing circulating fluids at disposals of drill fluids, cuttings, and formation water, the OP content in sediments can rise up to 50,000 μg/g (more than 50 GBVs) near and around SSP (from several hundreds meters to several kilometers). Such a situation was observed in the North Sea (Dutch shelf, 1985–1992), where > 1 million t of drill cuttings polluted bottom sediments with OP within the 8,000-km^2 area, were disposed.

According to the 1987–1993 monitoring data, the content of OP in sediments of the Karkinit Bay (3.5 GBVs) corresponded to the degree of their pollution off Odessa and Sevastopol but it was 2–3 times higher than that observed earlier in the bay and in the Dnieper offshore zone. In extreme cases fixed during the monitoring period, the OP concentrations in sediments of the Karkinit Bay (11 GBVs) were more than 3 times as large as the sediment pollution of the Odessa coast and Sevastopol bays, where the situation in terms of this characteristic was the worst. The data on extreme pollution coincide with the examples from the practice of the world's oil hydrocarbon production on the continental shelves.

Microelements

The concentrations of Hg and Cd in bottom sediments near the SSP bases on the northeastern Sakhalin shelf and within 8 km from them vary from 0.017–0.03 and 0.01–0.05 μg/g that is much lower than the GBV for the Black Sea. In the Gulf of Mexico, the maximum concentration of Cd in bottom sediments near SSPs 6–12 years after the completion of exploratory drilling, did not exceed 0.006 μg/g that was 50 times lower than GBV for the Black Sea.

Compared to the results of analysis of the literary data on the pollution of Black Sea sediments with microelements, their concentrations in sediments of the Karkinit Bay, registered in the course of monitoring, in extreme situations in terms of Hg (1.8 GBVs) and Pb (9 GBVs) exceeded the values observed in those areas of the NWSH of the sea where the conditions were adverse in terms of these characteristics. The anomalies for Cu (1.1 GBVs) were lower than those in the coastal sites of the shelf, and the Cr concentrations in sediments in the zones of offshore gas production (up to 65 μg/g) were found to be much less than the GBV (84 μg/g) and, accordingly, less than the values of this characteristics in other more polluted areas of the northwestern shelf, the rest of the Black Sea coast (North Caucasus, Georgia), and shelves of the World ocean.

5.5.4 Hydrogeochemical Consequences of Offshore Gas Production

The analysis performed in this monograph allowed us to establish the hydrogeochemical consequences of the development of offshore gas fields on the northwestern shelf of the Black Sea and identify their following features:

Before the beginning of drilling operations on the NWSH from 1975 to 1984, the mean total water content of OP in the surface and near-bottom layers steadily exceeded the MAC by a factor of 10–20, having reached the maximum of 2,900 μg/g (58 MACs) in 1977; bottom sediment pollution could exceed the GBV 3 times.

By 1984, after the reinforcement of control regulations of OP transportation, water pollution in the Karkinit Bay decreased; however, the norm for mean values was exceeded by a factor of 2.5–4 and that for maximum values, by a factor of 4–6. The sources of OP pollution remained on the northwestern shelf of the sea. They could be associated with transportation and offshore hydrocarbon production.

After the beginning of exploratory drilling and in the process of commercial production of wells, within five years (1984–1989) the pollution of water column on the NWSH with OP in the SSP zones reached 14 MACs, while in the surface layer of bottom sediments (except for SSP bases) their concentrations decreased to 1.7 GBVs on the whole aquatory.

The maximum water pollution with OP (26.5 MACs on the surface and 42 MACs in the near-bottom layer) was fixed on July 30–31, 1989 in the *Karkinitskaya*-19 SSP zone after exploratory drilling. The extremely high total OP concentrations in that time were observed immediately at the drilling platform both on the surface (110 MACs) and near the bottom (265 MACs).

The maximum OP concentrations in bottom sediments were associated with the operating drilling platforms: *Golitsyno*-18 (6 GBVs), *Golitsyno*-2 (3.5 GBVs), *Golitsyno*-4 (13.9 GBVs), and *Shmidta*-6 SSP (11 GBVs) plugged and abandoned in 1990.

At the southern exploratory SSPs *Shtormovaya*-17 and *Arkhangelskaya*-7 which are subject to intensive advection of OP from the central part of the NWSH and from the South Coast of Crimea, the OP concentrations in sediments at well bases exceeded the GBV more than 2 times.

The lowest OP content in 1991 was registered in sediments of the inner part of the Karkinit Bay at the drilling SSP *Karkinitskaya*-19, which had been in operation for only one year and was remote from additional sources of OP. The OP concentration in sediments did not exceed here 460 μg/g.

The exploration and development of gas fields on the northwestern Black Sea shelf practically did not result in water pollution with Cu, Pb, and Cd, but the Hg and Cr concentrations in the surface layer of the SSP zone increased up to 5–7 and 2–3 MACs, respectively.

The maximum water pollution with Cr (28 MACs) was fixed in the near-bottom layer in March 1990, and the average concentration amounted to 4.5 MACs.

During the 1987–1993 period there was no anomalous cases of bottom sediment pollution with Cr on the NWSH of the sea.

Among all toxicants, the GBV in the surface layer of sediments was first exceeded by Cd (2.5 GBVs, July 1989), next by Pb (about 2 GBVs, July 1990), and since August 1992, by Hg (1.8 GBVs) and Cu (1.1 GBVs). The extreme pollution of bottom sediments with Pb (9 GBVs) and Cd (8 GBVs) was noted in August 1992 and September 1993.

5.6 Features of Offshore Hydrocarbon Fields Development Technology

To explain the obtained pattern of temporal and spatial variability of the environmental pollution in the zone of development of offshore gas fields on the NWSH of the Black Sea, we have analyzed the available data on the technology of offshore gas exploration and production and its features in terms of its possible impact on the hydrogeochemical regime of the sea (Patin 2001; Mitina and Singh 2005).

The major sources of sea pollution at the stage of exploratory offshore drilling are *drill mud* (anticorrosion washing fluids) and *drill cuttings* (rock fractured by drill). The commercial development of wells is accompanied with appearance of *formation water*, the most abundant type of waste and source of pollution associated with offshore hydrocarbon production.

Drill mud. Most drill muds now in use are water-based (up to 80–90%). However, in some cases known in the world practice of exploration of hydrocarbon fields on the oceanic shelf, inclined wells (with a deviation of up to 5 km from the vertical) or horizontal wells (to enhance extraction) were drilled in hard rocks. In such cases, *oil-based fluids*, which have high antifriction properties, are used. In the 1980s, such drill muds (emulsion mixtures containing up to 60–70% of OP, suspension of clayey minerals (10–20%) inorganic salts of Ba, Na, Ca, and microquantities of organic compounds) were used in 20% of cases for drilling of several thousands of exploratory wells in the Gulf of Mexico. In 1992, they were also used in 50% cases the North Sea that resulted in a significant pollution of water and sediments of the sea.

Photo 5.9 Base of drilling platform (*top*) is set (submersed) first on-site of future well, at which then the “roof” is attached (*bottom*) (Photo by V.Pishchalnik)

The disposal of water-based mud per one well during drilling on the Sakhalin shelf amounted to 500–1,000 m^3. The total disposal of waste drill muds in the process of drilling of wells with a depth of up to 5,000 m at the exploratory stage can reach 3,000–4,000 t, and that for production wells is by 25% lower. The daily disposal in this case is relatively slow (20–30 m^3/h); however, at the replacement of solutions (1–2 times a month) the large amounts of wastes are discharged within a short period (up to 50–150 m^3/h) (Photo 5.9).

At the offshore production of hydrocarbons in the Gulf of Mexico the main environment pollutants around drilling platforms are oil products and heavy metals. Their concentration are maximum in coarse deposits and decreased sharply as far as 100–200 m from a platform, but the pollution of benthic organisms is kept for several years (Mitina and Singh 2005).

In 1999 г, the OP concentrations in seawater in the zone of exploratory works in the North Caspian reached 46 MACs. With that, the content of aromatic hydrocarbons in Caspian gobies inhabiting the zones of drilling platform bases was 33.6 μg/kg, and 50% of individuals of sturgeon and sevruga stocks living in the area of offshore exploration and production of oil were characterized by resorption of gonads, i.e. they have the impaired reproductive function (Mitina and Singh 2005).

Drill cuttings produced at drilling of wells with the use of oil-based drill mud can contain, even after washing, up to 100 g/kg of OP (100 GBVs). Depending on the dimensions of well, the amount of cuttings during its drilling amounts to 500–1,000 t. At drilling of some wells the effects of pollution with drill cuttings are localized within a radius of 100–200 m from their bases. The radius of polluted zone in the case of many-year drilling increases to several kilometers. The volume of drill cuttings disposed into the sea in the process of drilling of one well (within 1–2 months) usually amounts to 200–500 m^3 (Sakhalin), i.e., 10–20 m^3/day (Patin 2001).

Formation water is a high-salinity fluid with complex chemical composition containing residuals of crude oil, organic acids, heavy metals, and other substances. As compared with oil fields, formation water of gas fields contains the higher concentrations of OP and microelements with a wider range of variations in their absolute values. These characteristics are different for each field. Before the discharge into the sea, the formation water is treated to remove OP. Nevertheless, the OP content in such water can reach 20–40 mg/L in fields of the North Sea, 9–230 (!) mg/L in fields on the Australian shelf, and 7–8 mg/L on the northeastern Sakhalin shelf. Thus, these water are 800, 4,600, and 16 times, respectively, more toxic than natural waters polluted up to the MAC (50 μg/L). Formation water disposed daily from wells of only one production platform in the Gulf of Mexico (160–223 thousand L) can contain up to 2 kg of oil products (Mitina and Singh 2005).

The concentration of Hg in formation water ranges from 0.05 to 12 μg/L; the concentration of Cu, from 1 to 30; Pb, from 1 to 50; Cd, from 1 to 500; and Cr, from 0.001 to 200 μg/L. In other words, such water can be 120, 6, 5, 50, and 200 times as toxic as natural waters polluted by these metals to the MAC level, respectively.

The volume of formation water disposed into the sea at the development of gas fields (1.6–30 m^3/day) is much less than that for oil production (2,400–40,000 m^3/day). The concentrations of Hg, Cu, Pb, Cr, and Cd in drilling zones of the Gulf of Mexico exceeded the background values for the sea by factors of 100, 1,000, 100,000, 750, and 5,000. The respective factors for the North Sea were equal to 1,000, 800, 10,000, 500, and 4,000.

The disposed formation water is diluted hundreds of times at the SSP base, and at a distance of 100–1,000 m from the platform, the degree of its dilution amounts to 10^3–10^4 times. The data for the Norwegian shelf show that the dilution zone of formation water to the sublethal level for planktonic organisms (0.1–1%, or by a factor of 100–1,000) can extend over a distance of several miles from the platform, with the peak of concentration at depths of 25–50 m. Zones of oil pollution are formed in the areas subject to the long-term disposal of formation water; however, their size and OP concentration in sediments in this case are much lower than those in the case of discharge of oil-containing cuttings and waste oil-based drilling mud.

5.6.1 Normative Legal Regulation of Offshore Hydrocarbons Exploration and Production

Now, there is no a separate legislative document in the world's practice of normative legal regulation of the development of offshore oil-and-gas fields (Patin 2001). Each government solves such problems in its own way, taking into account the common environment-oriented principles and specific conditions either existing in the country itself, or determined within the framework of provisions of universal (global) international conventions. Thus, in the late 1980s, after the oil boom in the North Sea, accompanied by its catastrophic pollution, the authors of Convention for the Protection of the Marine Environment of the North-East Atlantic recommended to forbid the use of oil-based drill mud for drilling in the upper horizons of wells and disposal in this case drilling wastes into the sea, as well as to introduce a limitation of 10 g/kg on the allowable oil concentration in the disposed drill cuttings. The provisions of the Convention were corrected and amended in 1992 and then in 2000. As a result, as early as 1996, most oil-producing countries in this region completely ceased the disposal of drill cuttings into the sea, thus reducing the input of OP into the marine environment by 60%, compared to 1985.

The authors of the similar Paris Convention 1978 recommended the maximum allowable levels of OP content in formation water within 20–40 µg/L. However, oil in formation water of the gas and gas condensate fields occurs commonly in the form of stable suspensions and emulsions and is difficult to separate. By this reason, the standards of formation water treatment for such fields, for example, on the shelves of the United States, Norway, Great Britain, and Australia vary in wide range (from 10 to 100 mg/l).

Because of the high variability and uncertainty of content of components other than oil in formation water, there is no any unified regulations for content of, for example, microelements both in national or international rules.

5.6.2 Possible Mechanisms of Environmental Pollution During Offshore Gas Production in the Karkinit Bay of the Black Sea

The field observations performed in this monograph allowed us to assess the oceanographic conditions in the zone of development of offshore gas fields and contribution of this process to environmental pollution of the NWSH of the sea. The data obtained are not of only practical interest as a basis for development of environmental protection measures and estimation of possible ecological consequences of this type of economic activities. Monitoring and subsequent analysis of results of offshore hydrocarbon production in other regions of the World Ocean allowed formulating the hypothesis about the possible mechanisms of environmental pollution during the development of offshore gas fields on the northwestern shelf of the Black Sea.

The study of the technology used to develop offshore gas fields allows us to conclude that the anomalous water pollution on the NWSH of the sea with OP during exploratory drilling at the *Karkinitskaya*-19 SSP in July–August 1989 is most probably associated with the use of inadvisable oil-based drill mud. The periodic disposals of 70% oil emulsion within a month and its one-time disposal after the completion of exploration could deliver up to 700 t of OP into the sea. This amount should be increased by 50 t of OP that entered the sea in this case at the discharge of even minimum amount (500 t) of drill cuttings with OP concentration of about 100 g/kg. As a result, there was a sharp increase in the OP concentration in the water column. The similar technological causes can explain the fact of increase in OP concentrations in sediments at the drilling *Shtormovaya*-17, *Arkhangelskaya*-7 SSPs, and at the *Shmidta*-6 well, which was plugged and abandoned after 5 years of operation.

The duration and development of the environmental pollution of the Karkinit Bay with microelements are obviously determined by both the terms of putting wells on production (the beginning of commercial gas production and, accordingly, formation water disposal without adequate treatment) and the chemical composition of formation water, specific for each well (e.g., predominance of Hg or Cr). However, one should also take into account the possible effect of the type of sediments (silts) at SSP and the advection factor, i.e., the OP transport by currents from the open NWSH areas affected by river runoff, and from the South Coast of Crimea, where water and sediment pollution with microelements is rather high.

Moreover, the cases when the maxima of water and sediment pollution in the bay are not associated with well bases, as well as the presence of areas with the higher toxicant concentrations beyond the SSP zones (the northern part of the bay off the Dzharylgach Island coast with increased Hg, Cu, and Cr concentrations; the southern part of the shelf near the continental slope and off Cape Tarkhankut with the higher Hg and Cu content; the northern coast of Cape Tarkhankut with the higher Pb and Cu concentrations) show that the formation of pollution fields in this area is also affected by other natural and anthropogenic factors. Obviously, they include the supply of pollutants with river water and their mobilization from bottom sediments under sand recovery near the Dzharylgach Island and bottom trawling fishery in the southern part of the shelf and off Cape Tarkhankut. Moreover, we cannot exclude the effects exerted on the dynamics of pollution fields by the accumulating factor of quasistationary anticyclonic eddy on the continental slope of the NWSH of the sea, wind activity over the shelf aquatory (waves), and the pattern of drift currents in the bay. Finally, the intensity of OP biotransformation and sorption characteristics of sediments and hydrobionts, depending on many physicochemical conditions undoubtedly affect the distribution and state of environmental pollution in the development zones of gas fields.

5.7 Mathematical Modeling of Oil Product Transformation in Karkinit Bay Waters on the Basis of Geographic and Ecological Data

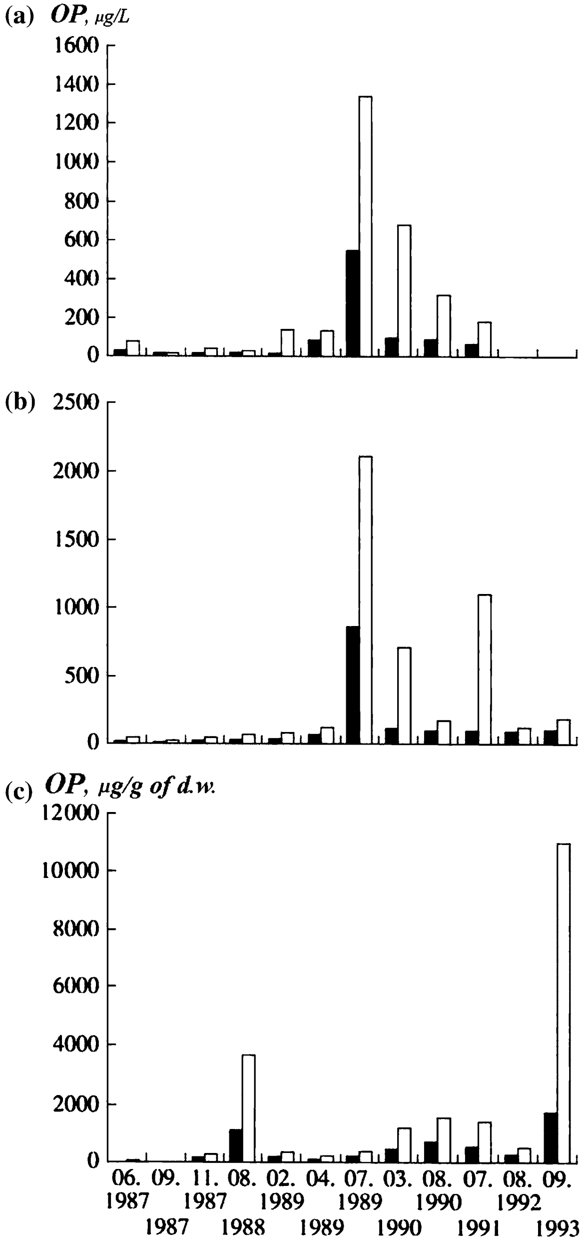
The results of monitoring and geographic and ecological modeling of the northwestern Black Sea shelf were used as an information base for the study of reality of the suggested hypothesis about the causes of catastrophic pollution of Karkinit Bay water with oil products (256 MACs) on July 30–31, 1989 at the *Karkinitskaya*-19 SSP (Fig. 5.15) with use of mathematical modeling (Leonov and Fashchuk 2006). Moreover, the mathematical model allowed us to investigate the mechanism of self-purification of the Karkinit Bay from oil pollution under the influence of hydrodynamic and biochemical factors (Fashchuk et al. 2006b).

From the analysis of experience of offshore hydrocarbon field development, it is known (Fashchuk et al. 2003) that in case of chronic pollution of the sea, after evaporation of volatile fractions, aggregation (5–10%), and sedimentation (10–30%), OP, finally, remain in water in form of solution or emulsion. Thus, their eventual fate depends on hydrodynamic (advection by currents), chemical (oxidation), and biochemical (bacterial degradation) processes which determine, in whole, the self-purification potential of the sea.

The compilation of data on the role of biochemical degradation of OP in marine environment showed that the share of their bacterial oxidation can amount to 20–98%, subject to conditions (Tsyban and Simonov 1978). The rate of oil degradation ranges from 35 to 350 g/m^3/year (Artyukhin and Nosov 1987). It takes 2–3, 2–10, and 100 years for the complete environment recovery due to biochemical OP transformation in tropical, temperate, and polar latitudes, respectively (Konovalov et al. 2004). According to other data, the time scales of oil biodegradation in its offshore production zones vary from one week to one year (Patin 2001).

According to the results of geoecological modeling (Egorov and Fashchuk 2003), the water exchange between the northwestern shelf and open Black Sea depends on wind conditions over its aquatory and occurs most intensively under the wind flow of north quarter, which maximum frequency (25–28%) is observed in winter, while in other seasons it does not exceed 8%. Moreover, in November 1978, the specialists of the former Sevastopol Branch of State Oceanographic Institute (GOIN), as a result of instrumental observations on currents at buoy stations at the section from Cape Tarkhankut to the Danube (Atsikhovskaya 1977), have established that under winds of north quarter with speed of 10–15 m/s, the daily water exchange volume through the lateral plane of the cross-section amounted to 3.7% of the total shelf water volume, while under the weak unsteady winds only 0.6% of NWSH water was renewed. In summer months, when frequency of such winds is minimum, according to data obtained during the similar investigations in the late 1960s, under light air and weak winds of other directions, only 4 km^3, or 0.4% of the total shelf water volume, can be renewed per day.

Fig. 5.15 Dynamics of oil product concentrations in the Karkinit Bay in 1987–1993 (Fashchuk et al. 2006b). **a**, **b** Surface and near-bottom water layers; **c** bottom sediments



Thus, the area under investigation in terms of dynamics represents a unique "trap" for polluted waters. The role of hydrodynamic mechanism of their purification from OP seems less important here, compared to the processes of biochemical OP transformation.

20 years ago the investigators of activity of oil-oxidizing bacteria in the Black Sea suggested that within the 100-m isobath these organisms could oxidize about 2,000 t of OP annually. With that, because of complexity of the OP biotransformation mechanism, the scientists cast some doubt on the possibility of its mathematical modeling (Mironov 1985). The further results of laboratory studies showed that, indeed, it was difficult to apply the apparatus of mathematical modeling for these purposes because of the established diversity of factors affecting kinetics of chemico-biological oxidation of hydrocarbons and a lack of any strong relationships between the abundance of oil-oxidizing bacteria and their activity (Ilyinsky 2000).

Nevertheless, some papers published in the beginning of the XXI century, showed the possibility of modeling of biochemical OP degradation and, in particular, the light, intermediate, and heavy fractions of oil in the Black Sea at different depths in the 0–200 m water column, taking into account their ratio at different depths and intensity of supply sources (rivers, atmospheric precipitation, exchange via the Bosporus). The temperature effect on the degradation rate of OP fraction under the influence of oil-oxidizing microflora is also taken into account. The abundance of the latter is set constant over the aquatory and equals 1,000 cells/mL of water. The model, thus, reproduces the conditions of concentration dynamics for different OP fractions in the anaerobic layer of the sea and identifies the spatial differences in their distribution, depending on the presence of supply sources (Konovalov et al. 2004).

Certainly, this approach deserves attention and further development, though, in our opinion, it has some essential faults. For example, according to the literature data, the abundance of oil-oxidizing bacteria in the Black Sea is not constant. Normally, it changes both in time and space (depth, sea area) within several orders of magnitude; at the marine environment pollution with OP the abundance of oil-oxidizing bacteria can increase by a factor 10^3–10^5 in 2–5 days. Moreover, the first-order chemical equation representing the process of OP fraction degradation in the model does not reproduce the adaptation period of microflora to pollution, as well as the sharp changes in OP concentrations under the maximum activity of oil-oxidizing bacteria, which are observed at natural conditions not infrequently.

In this context, after the analysis of existing experience of the marine basin study by mathematical methods (Fashchuk et al. 2005), we solved the posed problem with the use of simulation box hydroecological model of OP transformation in marine environment (see Sect. 2.3.5).

5.7.1 Input Data and Scenarios of Numerical Experiments

In accordance with the described model structure, the data, necessary for the beginning of calculations, include information about the morphometric characteristics of the area under investigation, its water exchange with the adjacent aquatories; monthly values of hydrometeorological parameters and characteristics of hydrochemical regime, determining the intensity of biochemical processes; background values of water oil pollution and volumes of toxicant flows from the external sources (river runoff); and the typical dependences of biomasses of organisms participating in chemico-biological transformation of organogenic compounds, on the number of substrates and conditions of their consumption.

The total area of the Karkinit Bay is 3,100 km^2, water volume, 54 km^3, mean depth, 16 m. At the gas exploration drill muds are disposed into the sea pointwise, immediately near SSPs, and pollution of aquatic environment is observed within a radius of 1.5 km (Pankratova et al. 1993). In this context, to model the dynamics of oil pollution, we estimated the water mass volume, in which the pollution effect was noticeable and, correspondingly, the OP transformation was performed, in 0.113 km^3.

Taking into account the features of wind activity over the aquatory under investigation and dynamics of shelf waters, when modeling, it was supposed that on a monthly basis about 10% of the bay water is involved in water exchange with the adjacent shelf aquatories. Moreover, according to the same data, the influence of pollutant discharge with Danube waters on the bay water pollution was set maximum in winter months, when the maximum (20%) frequency of SW winds was observed. In other months of the year, the contribution of this factor was 3 times lower because of a decrease in frequency of south-quarter winds to 8%.

The background water pollution of the Karkinit Bay with OP is assumed to be equal to 200 μg/L, based on the earlier made generalization on the pollution of northwestern Black Sea waters (Fashchuk et al. 1995), used at development of the information model—“portrait” of the NWSH of the sea (see Sect. 5.1). The nutrient content in the Danube runoff is taken from the paper (Berlinsky et al. 2004**)**. The mean long-term monthly values of parameters of hydrometeorological and hydrochemical regimes of bay water are set by the results of our and literary generalizations (see Sect. 5.1.2). Some of them are presented in Table 5.6.

The lowest mean long-term water temperature in the Karkinit Bay is observed in January (−0.1°C), whereas the warmest month is July (24.4°C). Water transparency is the least in March (6.7 m) and the largest in November (12.8 m). The light intensity is the least in December (77 cal/(cm^2 day)) and the largest in July (584 cal/(cm^2 day)). The precipitation volume is minimum in March (0.0903 km^3) and maximum in December (0.1674 km^3). The shortest light day is observed in December January ($f = 0.34$) and the longest in June ($f = 0.64$). The maximum Danube runoff is noted in May (26.33 km^3/month) and the minimum in October (10.74 km^3/month).

To simulate the situations of environmental pollution in the SSP area, 13 numerical modeling experiments have been performed. In the first of them (test), the mean long-term monthly values of input parameters describing the conditions of nutrient and OP discharge into the marine environment with the river runoff and from the background pollution sources have been put in the model. By these data the intraannual variations in nutrient and OP concentrations, biomasses of planktonic organisms and oil-oxidizing bacteria were reproduced by means of the model. The calculated concentrations of substances were compared then to the

Table 5.6 Mean long-term monthly values of environmental parameters (N) for aquatory of the Karkinit Bay of the Black Sea (Leonov and Fashchuk 2006)

(N)	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
t	−0.1	0.0	3.5	11.3	18.3	22.3	24.4	23.6	19.3	12.9	6.9	2.1
ds	8.0	6.8	6.7	7.3	8.6	9.3	9.5	9.9	11.0	12.3	12.8	10.8
R	90.2	142.5	261.2	403.6	519.3	576.4	584.0	493.1	373.4	219.6	100.3	77.0
pr	0.1364	0.1302	0.0903	0.0930	0.1085	0.1209	0.1023	0.0992	0.1085	0.1085	0.1333	0.1674
f	0.34	0.41	0.49	0.59	0.64	0.69	0.67	0.60	0.52	0.44	0.36	0.34
q	15.0	14.76	19.93	24.36	26.33	20.37	17.47	13.23	10.85	10.74	12.00	14.48

t is water temperature, °C; *ds* is transparency, m; *R* is total light intensity, cal/cm^2 per day; *pr* is atmospheric precipitation, km^3 ; *f* is photoperiod; *q* is the Danube runoff, km^3

available literary data on their dynamics (Project "The Seas …" 1992), and in case of their lack, to indirect indicators of one or another process. For example, the available experimental data on oxygen consumption under OP oxidation (Tsyban and Simonov 1978) were used as indirect criteria of correctness of the description (formalization) and reproduction of OP degradation rates by the model. The full degradation of 1 kg of oil requires oxygen containing in 400 thousand L of sea water. For full oxidation of 1 mg of oil 3–4 mg of oxygen are necessary, and full oxidation of 1 ml of oil requires 3.3 g of O_2 (Kostrov et al. 2000). Thus, during the first numerical experiment we tested the adequacy of modeling calculations and assured ourselves of the possibility of further model use for the prognostic purposes.

In the next twelve numerical experiments, the scenarios of point pollution of the sea, with OP disposals of 1,000, 500, and 200 t within a week (as it was assumed in the investigated hypothesis) during different seasons of the year (winter (February), spring (April), summer (July), autumn (November)), have been realized. The model reproduced the intraannual dynamics of OP concentrations (Fig. 5.16). The calculations were made for the period from January, 01 to December, 31. In the scenario of autumn disposal, purification of the sea by the end of the year did not occur, therefore the calculations were prolonged to the next year under conditions of OP discharge into the water, similar to those in the test experiment (with the river runoff and from the background sources). The intermediate results of calculations (terms and concentration values) for each scenario were printed and combined in summary prognostic table of OP content dynamics, with account of the development of bacterial oxidation processes in the environment and advection of the different-scale drill mud disposals in the offshore gas exploration and production zone in the Karkinit Bay by currents (Table 5.7).

5.7.2 *Calculated Dynamics of Oil Products Concentrations and Forecast of Time Period of Shelf Water Self-Purification from Oil Pollution*

As a result of the series of model calculations, we obtained a simulated pattern of Black Sea shelf water *pollution* at different volumes and terms of drill mud disposals in the process of gas field development, and the subsequent *self-purification* of water masses under the influence of biochemical OP degradation and water dynamics.

5.7.2.1 Winter

During this season the activity of oil-oxidizing bacteria is minimum, and the process of self-purification of the sea is determined mainly by dynamic factors. In case of disposal of 1,000 t of OP into the sea from SSP within the first week of

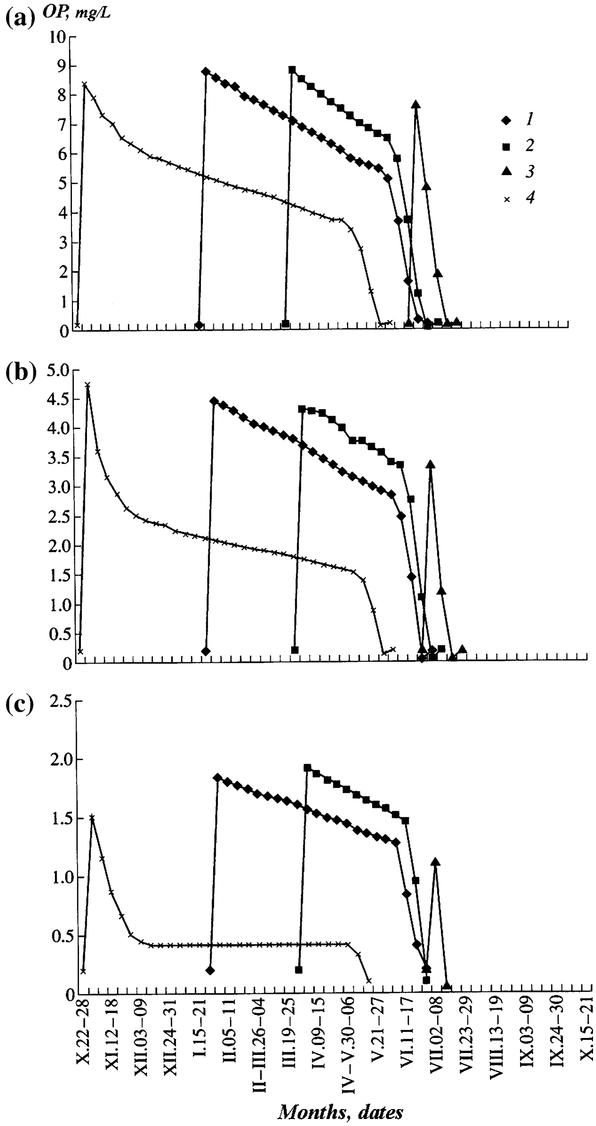


Fig. 5.16 Calculated annual dynamics of oil product concentrations in the area of gas field development on the northwestern Black Sea shelf under different scenarios of drill mud disposal (Leonov and Fashchuk 2006). **a–c**: Disposals of 1000, 500, and 200 t/week, respectively. *1* winter, *2* spring, *3* summer, *4* autumn

February, their water concentrations first increase up to 8.79 mg/L (176 MACs), and then, within 19 weeks (until the end of June), they decrease gradually to 5 mg/L (100 MACs). In July, with water warming, the intensity of biochemical processes increases sharply and during this month the OP content in water decreases

Table 5.7 Calculated dynamics of OP concentrations (mg/L) in the Karkinit Bay of the Black Sea under the influence of bacterial oxidation and advection of different-scale drill mud disposals in the offshore gas exploration and production zone by currents (modeling)

Period after disposal (weeks)	Volume of disposal (t/week)											
	1,000				500				200			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
0	8.79	8.82	7.62	8.40	4.45	4.31	3.36	4.75	1.83	1.91	1.11	1.51
1	8.58	8.50	4.82	7.90	4.37	4.27	1.20	3.60	1.80	1.86	0.06	1.16
2	8.37	8.25	1.87	7.30	4.29	4.23	0.06	3.16	1.77	1.81	**<MAC**	0.87
3	8.26	7.98	0.16	7.01	4.16	4.11	**<MAC**	2.88	1.74	1.77		0.66
4	7.95	7.73	**<MAC**	6.55	4.05	3.98		2.64	1.70	1.72		0.51
5	7.80	7.50		6.33	4.00	3.76		2.51	1.68	1.68		0.45
6	7.64	7.26		6.12	3.93	3.75		2.43	1.66	1.64		0.42
7	7.46	7.00		5.90	3.87	3.65		2.37	1.64	1.60		0.42
8	7.30	6.84		5.93	3.80	3.56		2.35	1.61	1.57		0.42
9	7.10	6.64		5.67	3.69	3.40		2.25	1.57	1.51		0.42
10	6.90	6.49		5.55	3.58	3.35		2.20	1.53	1.46		0.42
11	6.70	5.78		5.44	3.47	2.74		2.16	1.50	0.95		0.42
12	6.50	3.70		5.32	3.36	1.09		2.12	1.47	0.10		0.42
13	630	1.23		5.20	3.24	0.05		2.08	1.44	**<MAC**		0.42
14	6.10	0.06		5.08	3.15	**<MAC**		2.04	1.39			0.42
15	5.80	**<MAC**		4.96	3.07			2.00	1.36			0.42
16	5.67			4.86	2.99			1.96	1.33			0.42
17	5.57			4.77	2.91			1.93	1.30			0.42
18	5.48			4.68	2.84			1.91	1.28			0.42
19	5.09			4.59	2.48			1.88	0.84			0.42
20	3.67			4.50	1.44			1.85	0.41			0.42
21	1.64			4.34	0.05			1.80	**<MAC**			0.42
22	0.31			4.22	**<MAC**			1.75				0.42

(continued)

Table 5.7 (continued)

Period after disposal (weeks)	Volume of disposal (t/week)											
	1,000				500				200			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
23	**<MAC**			4.09				1.71				0.42
24				3.96				1.66				0.42
25				3.85				1.62				0.42
26				3.73				1.58				0.42
27				3.69				1.53				0.41
28				3.39				1.39				0.33
29				2.73				0.87				0.10
30				1.28				0.13				**<MAC**
31				0.14				**<MAC**				
32				**<MAC**								
Period to reach the MAC (days)	155	99	24	224	148	92	16	217	144	85	9	210

to the MAC value. It occurs 155 days after the cease of drill mud disposals (Fig. 5.16a; Table 5.7).

In case of the 500-t disposal of OP in the same season (Fig. 5.16b), their content in water increases up to 4.45 mg/L (89 MACs), in 18 weeks (to mid-June) it decreases slowly to 3 mg/L (60 MACs), and then within three weeks (to the beginning of July) it reaches the MAC value (148 days after pollution).

When winter OP disposal is 200 t (Fig. 5.16c), their concentration in water first increase up to 1.83 mg/L (36 MACs), and then within the next 18 weeks (by the mid- June) this value changes very slightly (1.28 mg/L, or 26 MACs). Further, within two weeks (by the end of June) there is a sharp decrease in OP concentration to the MAC t. In this case the self-purification of the sea requires 144 days.

5.7.2.2 Spring

During this period of year (the first week of April) the disposal of 1,000 t of OP into the sea also results in a sharp growth of their water concentration up to 8.82 mg/L (176 MACs). But, unlike winter, the further decrease in OP content to 5 mg/L (100 MACs) occurs much faster, within 12 weeks, because of the earlier (after disposal) entrainment of bacteria into their transformation. The further abrupt decrease in OP water concentrations occur, as in the winter scenario, within three weeks of July, and 99 days after the disposal (in the end of July) they reach the MAC values (Fig. 5.16a; Table 5.7).

The disposal of 500 t of OP in spring results in an increase in their water content up to 4.31 mg/L (86 MACs). Further, within 11 weeks (by the beginning of July) this value decreases to 2.74 mg/L (55 MACs), and then during the first two weeks of July (92 days after disposal) it decreases sharply to the MAC values. In case of the 200-t disposal of OP in spring, their concentration in water increases up to 1.91 mg/L (38 MACs), and terms of pollution degradation, as in the winter scenario, are shifted for a week. In this case, the self-purification of the sea occurs 85 days after disposal (Fig. 5.16c).

5.7.2.3 Summer

During this period the situation for self-purification of the sea from OP pollution is most favorable because of coincidence of the peak of microflora activity with the moment of OP disposal. After disposal of 1,000 t of drill mud into the sea within the first week of July, the OP content in water, as in the previous scenarios, increases sharply up to 7.62 mg/l (155 MACs). But as early as within the next week, biochemical transformation results in a twofold decrease in their concentrations here, and a week later they already amount to 1.87 mg/L (37 MACs). By the beginning of August, 24 days after disposal, the concentrations reach the MAC value (Fig 5.16a; Table 5.7).

In case of disposal of 500 and 200 t of OP in summer, their concentrations in water increase up to 3.36 and 1.11 mg/L (67 and 22 MACs), respectively. The self-purification of the sea and decrease in OP concentrations to the MAC values occur just in 16 and 9 days.

5.7.2.4 Autumn

In scenarios of autumn (the first week of November) disposals of 1,000, 500, and 200 t of OP, their water content increases sharply up to 8.40, 4.75, and 1.51 mg/L (168, 95, and 30 MACs, respectively). However, their discharge into the sea in this season coincides with the beginning of autumn water cooling and, correspondingly, with a decrease in activity of oil-oxidizing bacteria. For this reason, till the end of the year (Fig. 5.16) in the process of bacterial destruction the OP concentrations are able to decrease only to 5.90, 2.37 and 0.41 mg/L (118, 45, and 8 MACs). A complemented series of calculations has allowed to establish that in case of disposal of 1,000 and 500 t into the sea the further transformation of OP continued in winter and spring months of the next year, until the mid-June and the beginning of June, respectively (22 and 21 weeks). A sharp decrease in OP concentrations to the MAC values begins only from this moment. The self-purification of the sea in this case occurs during the first week of July and last week of June, respectively, i.e., 224 and 217 days after disposal.

The concentrations of oil products remaining in the sea by the end of the year (0.41 mg/L) after disposal of 200 t of drill mud almost do not change within 20 weeks of the next year. Only in the beginning of May within its first two weeks their sharp decline from 8 to 1 MAC is observed. The self-purification of the sea in this case occurs in 210 days.

5.8 Conclusions

According to the simulation results, the values of OP concentrations after their disposal in Karkinit Bay water in volumes of 1,000, 500, and 200 t within one summer week amount to 155, 67 and 22 MACs. These values coincide with the data of our field observations conducted in July 1989 at the *Karkinitskaya*-19 SSP, when OP content in water around the drilling platform was 26.5–42 MACs, and immediately at the SSP, 110–265 MACs (on the average 188 MACs in the layer from the surface to bottom).

Thus, the complex realization of information geographic and ecological model of marine basin (as source of input and test data) and hydroecological mathematical model of OP transformation (as apparatus for calculation) has allowed us to confirm a hypothesis that the cause of anomalous pollution of Black Sea shelf waters in the SSP area in the Karkinit Bay in July 1989 consisted in the use of oil-based liquid mud during the exploratory drilling and their disposal into the sea in the volume of 500–1,000 t.

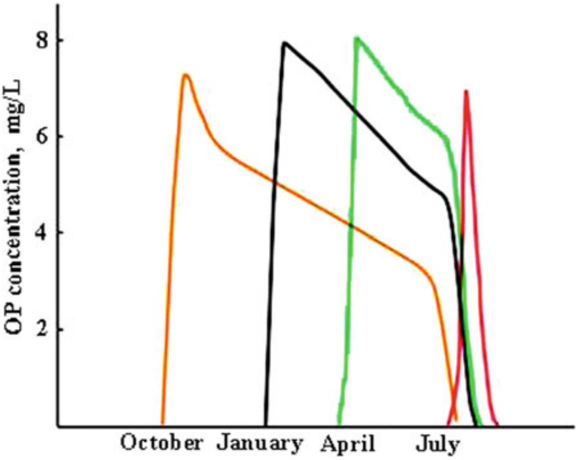


Fig. 5.17 Scheme of self-purification of the sea from oil pollution, depending on time of oil product disposal

Moreover, the model numerical experiments performed in this study have allowed us to make prognostic estimates of time, necessary for self-purification of the sea from oil products, depending on season and volume of their disposal. On this basis, the practical recommendations for selection of the safest modes of OP disposal during the exploratory drilling were developed. So, in the period of low activity of oil-oxidizing bacteria (winter, spring, autumn) the purification of the sea from OP occurs slowly (inclined plateaus in Fig. 5.17) and mainly due to their transport from the area by currents. Such prevalence of the dynamic mechanism of self-purification of the sea over the biochemical mechanism in these seasons continues during 18–19, 11–12, and 21–22 weeks, respectively. Only by July, with water warming and activation of oil-oxidizing bacteria a sharp (within 2–3 weeks) decrease in OP concentrations to the MAC values occurs.

Thus, autumn is the most unfavorable season for OP disposal into the sea (conduct of exploratory works). In case of drill mud disposal during this period in volumes of 1,000, 500, and 200 t within a week the total time of their transformation to the MAC value under the influence of joint effect of water dynamics and biochemical factors is 224, 217, and 210 days, respectively. At the small volumes of disposals, by the end of the year and during the winter–spring season of the next year the OP supply into the SSP zone with river runoff and from background sources and their transport outside the area by sea currents are canceled out (horizontal plateau in Fig. 5.16c for disposal of 200 t/week), and self-purification of the sea prior to the beginning of summer warming does not occur. The sea is purified from OP most rapidly in case of their disposal at the time of the maximum activity of oil-oxidizing bacteria, i.e., in summer. Under the drill mud disposals of 1,000, 500, and 200 t/week it occurs in 24, 16 and 9 days, respectively.

The above-cited example of use of the mathematical model ensured with the adequate information, for solving of the concrete practical problem confirms the necessity of further strengthening of a role of constructive geography at realization of the large economic projects associated with exploitation of natural resources. The arguments for scientific rationale of environmental protection measures and practical recommendations to economic managers should not be based only on the *diagnostic information* (data of field observations). The necessity of wider use of *prognostic information* in practice of geographical science is obvious. This information can be obtained only under a close cooperation of geographers with experts of existing advanced (on the global scale) schools of mathematical modeling. The success of cooperation, making right decisions, in addition to material resources, depends also on sincerity of scientists' desire to understand the nature, and, therefore, on their ability to listen each other attentively.

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Chapter 6
Geographic and Ecological Assessment of Coastal Zone on the Russian Black Sea Aquatory as a Region of Mariculture Development

From ancient times the ocean was the major source of food for mankind. Throughout many millennia of existence of our civilization its biological resources were considered as the inexhaustible. In the seventeenth century Dutch scientist–lawyer Hugo Grotius by working on principles of economic development of the World Ocean fondly believed that "the sea cannot be exhausted neither owing to sailing, nor owing to fishing, that is any of ways with which it can be used." However, soon the world was convinced of an inconsistency of this concept of ocean as "RES COMMUNIS"—things belonging to all. Having killed fur seal stocks in the span of just a few years, in 1911 the heads of leading powers—the USA, Russia, Japan and Great Britain (Canada)—have entered into the first agreement in the history of a marine law on protection of ocean resources (Slevich 1977).

The rapid growth of the World's population was accompanied by intensification of its activity on development of marine biological resources. From 1950 to 1970, the rates of world fisheries catch growth increased annually by 10%, exceeding rates of an increase in population of the Earth. If in the middle of the last century the total world catch of fish and seafood was only 17 million tons, by 1970 it has increased by factor of 5. But before the 1990s the catch volume was stabilized, having reached the level of 95 million tons, as it became obvious that commercial stocks of fish and other seafood were limited and exhausted, and the fishing level reached its maximum allowable value (Pshenichny 2005).

In the early twenty-first century, despite the stabilization of world catch volume, its value, nevertheless, has exceeded 130 million tons. This growth was associated with an active development of aquaculture. The volume of its world production today amounts 35 million tons, or more than 30% of total world production of seafood. The development of managed marine farms for production of protein food started worldwide since the 1980s, is now the most promising direction in use of biological resources of the World ocean (Pshenichny 2005).

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In 2006, in the Black Sea on the beam of settlement Khosta (the Big Sochi), at distance of 2.6 miles from the coast and at depth of 40 m the installation of underwater farm for rearing of mullet, trout, and steelhead trout has been started (Photo 6.1).

The underwater automated fish-rearing ponds of farm (PARS) consist of the top and bottom hexagonal frames with the adjustable buoyancy, executed of steel pipes between which the net chamber is fixed. In the centre of the top frame the feed tank, feed dispenser, and pond control system are located (Photo 6.2a). The operating position of pond is underwater. To the top framework of pond the replaceable ballast plastic (metal) cisterns ensuring immersion and emersion of construction at their filling with water or compressed air as required are attached.

The design of pond PARS-2500 allows to expand the volume of net chamber from 1,200 to 4,000 m^3. In underwater position it survives a storm with the maximum wave height (for the Black Sea) and currents up to 2.0 m/s. In position afloat (Photo 6.2b) the system is served at force-three wave. PARS is kept on the ground by three gravitational anchors located in corners of equilateral triangle with side of 100 m at depth of aquatory down to 50 m. The total area of farm is 6 ha (100 × 600 m).

Photo 6.1 During the freshwater period of life cycle all salmon species are called "trout" (**a**). On the American coast of the Pacific Ocean salmons of Mikizhi (*Parasalmo*) genus are named "rainbow trout" (lake form) (**b**) or "steelhead trout" (marine form) (Photo by A. Konovalov)

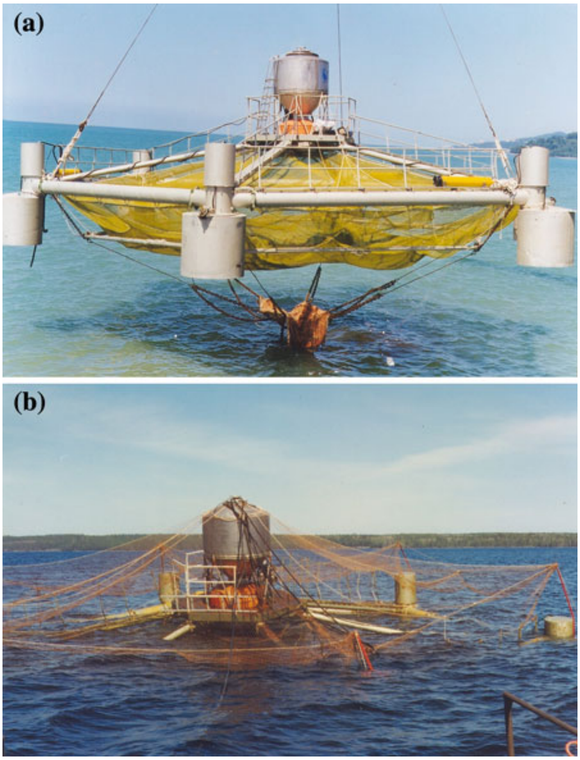

Photo 6.2 Automated fish-rearing pond PARS-2500 in surface position (**a**) and afloat (**b**). Photo by W. Muravyov

The tank containing 1.5–2.5 t of granulated feed provides autonomy of construction up to 25 days. The program controls feeding process, immersion and emersion of pond. The feeding time is set automatically, the dosage and frequency of feeding is ensured. At the moment of feeding the bottom hatch of tank opens, the feed is released, and the hatch closes. At an increase in current speed up to critical values (2 m/s) the feeding is terminated to avoid of losses. The productivity of farm ensuring immersion and emersion of construction at their filling with water or compressed air as required are attached.

The productivity of farm is 300–500 t of fish per year (Photo 6.3).

The geographic and ecological information model—“portrait” of the North Caucasian coast of the Black Sea has been developed for estimation of possible adverse effects of operating fish farms on marine environment.

6.1 Features and Prospects of Mariculture Development in Russia

The systematization of data on development of mariculture in Russia (Dushkina 1998) has allowed to establish that its first stage concerns the 1970–1990 period when, following the world’s tendencies, in the seas washing the coasts of the

Photo 6.3 In 2007 the first commercial lot of salmons (2,000 kg) was produced at fish farm near Khosta (Photo by V. Muravyov)

former USSR in the north, the Far East, and the south (Baltic, Barents, White, Okhotsk, Japan, Black, Azov, Caspian Seas) the investigations and industrial developments on new direction in domestic scientific and fishery activity, artificial cultivation of fish, mollusks, and seaweed, started to develop. Till 1980 production of the Soviet aquaculture was not reflected in the world statistics. Nevertheless, by 1991 it has reached 438,000 t (1.1–1.3% of the world production). With that, it consisted basically of carp (freshwater) species. After disintegration of the USSR (detachment of Ukraine, Estonia, Latvia, Georgia), this value in Russia has decreased down to 78,000 t (1994), of which a share of mariculture (marine cultivation) was only 6,000–7,000 t (basically, seaweeds of the Sea of Japan). According to the latest data, the share of artificial cultivation of fish in our country accounts for 2% from the total volume of seafood, while in the world volume it has already reached 35%, and in China—50%.

Due to physico-geographic and climatic features of the Russian seacoast (exposure to winds and waves, relatively low temperatures, high variability of salinity), at organization of marine farms there it is not always possible to use technologies of other countries, for example, the experience of salmon rearing in the wind-protected fjords of Norway or cultivation of shrimps and tilapia in the warm seas of Southeast Asia. Besides, together with the traditional directions of mariculture development in Russia (cultivation of sturgeons and salmons), acclimatized ecdemic species—Far East pink salmon in the White and Barents Sea, Far East haarder in the Black and Azov Seas, Kamchatka crab in the Barents Sea, American striped bass in our southern seas—became mariculturally important in our country.

In the mid-1990s the cultivation of mussels in the White Sea and turbot in the Black Sea was defined as a priority direction of mariculture development in Russia. Moreover, in the White Sea the works on rearing of wolfish, laminaria, herring, and acclimatization of pink salmon are conducted. In the White Sea gulfs it is possible to rear up to 15,000 t of salmons, 10,000 t of mussels, and to 5,000 t of seaweeds (Dushkina 1998).

In the Barents Sea the commercial rearing of salmons (trout, Atlantic salmon, coho salmon), acclimatization of species introduced from the Far East (pink salmon, greenling, crab), cultivation of aboriginal species (cod, flounder, etc.) and commercial seaweeds and mollusks seem prospective.

In the 50-mile coastal zone of the Okhotsk and Japan Seas in Primorski Territory, on Sakhalin and Kurils, it is possible to get up to 5–6 million tons of mariculture production, including fish (salmons, mullets, ordinary fish), mollusks (sea scallops, mussels), invertebrates (trepangs, sea urchins, cucumaria, grass shrimps, crabs, etc.), seaweed (Dushkina 1998).

In the Azov–Don basin the cultivation and artificial reproduction of diadromous and semidiadromous fish is planned, and, also, Far East haarder is successfully reared there. In the Black Sea, despite a sharp decline in mariculture production (80–90%) in the 1990s, there is a hope of its recovery due to pond rearing of salmons (trout, steelhead salmon), sturgeons, cultivation of mussels and oysters, turbo, rearing of aboriginal grey and golden mullets.

In the end of the twentieth century all these plans have allowed to estimate the future growth of mariculture production in Russia in 200,000–300,000 t, a third of which consists of valuable fish species. Today in the country 115 private and state fish-farming companies rearing 25 species of fish and seafood, first of all, carp, trout, and sturgeon, operate in this direction. In 2005, the whole Russian aquaculture market was estimated in 200 million USD (the world market-in 35 billion USD). On the conclusion of Expert Institute under the jurisdiction of Russian Union of Industrialists and Entrepreneurs at a quite real 5–6-fold increase in volumes of fish catch and cultivation in inner water basins (up to 1.3–1.5 million tons, or 30–50% of total volume), this market can be grown up to 500 million dollars (Fish in incubator 2005).

6.2 World Experience in Estimation of Ecological Consequences of Fish Farm Functioning

At rearing of salmons in marine ponds, the products of their live activity and feed losses are the major sources of impact on environment. Thus, the character of water and bottom sediment pollution depends mainly on technology of feeding, feed quality and type. In Sweden, for example, at commercial rearing of salmons, in the area of fish farm installation (usually, these are calm, ecologically safe fjords and bays protected from winds) about 1–5% of dry, 5–10% of paste-like, and 10–30% of wet feed get into marine environment because of their incomplete use (Muravyev 2002).

In England, in the process of rearing of 15,000 t of salmons in 1990, at average value of feeding ratio (ratio of feed amount in kg per day to 1,000 kg of fish) equaled to 1.5, over 300 t of phosphates has got into environment. After the analysis of process technology it has been found that at transition to high-energetic feed with low phosphorus content ($\sim$1%) and at feeding ratio of 1.2, the phosphoric pollution can be lowered by 75%.

The most stringent requirements to quality of water flowing out of marine fish farm are specified in Denmark. It should contain not more than 1 mL/L of organic matter, 3 mg/L of suspended substances, 5 mg/L of phosphorus, 40 mg/L of ammonia, 60 mg/L of total nitrogen.

The underwater fish ponds "PARS-2500," which are supposed to equip a farm, have volume of 2,500 m^3 containing 60–100 t of fish during rearing. For large individuals (last stage of rearing), at 15°C the daily growth of body weight can be 0.9% from total weight, or in terms of the whole pond—up to 150 kg. At feeding ratio of 1.2 it will need 170 kg of feed per day, and at feeding ratio of 1.5–225 kg of feed.

The feed suggested for use contains 1% of phosphorus, while its content in fish body is 0.4%. Thus, at using of 225 kg of feed, out of the total 2.25 kg of phosphorus, 0.9 kg will be assimilated by fish, and 1.35 kg *of phosphorus will enter into the sea*. It is easy to make similar calculations for nitrogen, the content of which is equal to 7.5% in feed and 2.7% in fish body. In this case, marine environment will get *more than* 10 kg *of nitrogen*. Taking into account the fact that at production of 1 t of salmon about 1,200 kg of dry granulated feed is consumed, the environment gets about 12 kg of phosphorus, 65 kg of nitrogen, and 500 kg of organic matter.

After dissolution in water the products of fish metabolism and feed residues accumulating in location of farm become a source of nutrients for lower water vegetation (phytoplankton). Their non-dissolved part is concentrated on the bottom. Depending on the biotechnology of feeding, at production of 1 kg of salmon or rainbow trout, about 0.5–0.7 kg of waste as fecal pellets and feed residues are accumulated under marine pond. At the initial stage of farm operation, a number of benthic organisms are developed, using these organic sediments under ponds.

To investigate the possibility of development of such events off the coast of the Big Sochi, we have analyzed the natural factors determining supply and rates of biogeochemical transformation of organic compounds, conditions of sediment accumulation and ventilation of coastal waters.

6.3 Natural Factors and Mechanisms of Formation of Environment Conditions in Russian Coastal Waters of the Black Sea

Analyzing the world experience of marine fish farm exploitation, the priority natural and anthropogenic factors determining safety and efficiency of mariculture object rearing have been identified.

6.3.1 Physico-geographic Features of the North Caucasian Coast of the Black Sea

The Russian territorial waters in the Black Sea wash the coast of Krasnodar Territory, from Kerch Strait to border with Georgia (Psou River). The extent of Russian Black Sea coastline is about 400 km—less than 10% of the total coastline length of the sea (4,431 km). Among them, 309 km are subject to abrasion-slide, rock-slide, and landslide processes and characterized by similar types of coast. Only 60 km of the Russian Black Sea coast are represented by accumulative forms of relief: Spits, barrier beaches, accumulative terraces. The technogenic coasts get an increasing extension there also (Shakhin et al. 2001).

The area of marine fish farm construction is located in the Big Sochi area occupying coastal strip with length of almost 150 km. It stretches from the south to the north from Psou River to Shepsi River. Between these rivers, directly in the Big Sochi territory (settlements Makopse, Ashe, Lazarevskoye, Matsesta, Khosta, Adler, Veseloye) the small rivers: Mzmyta, Kudepsta, Khosta, Dagomys, Psakhe, etc.), run into the sea. Besides, in Georgia located to the south of Krasnodar Territory, there are the larger coastal rivers: Rioni, Chorohi, Inguri, Kodori, Bzyb, Supsa, etc., contributing annually up to 43 km^3 of fresh water (12.7% of a total river discharge into the Black Sea) and, certainly, affecting the marine environment state in the area of fish farm installation (Table 6.1).

Off Big Sochi the shelf width (down to the 200 m isobath) is 4–12 km. Here, it has a flat plain surface with slope of 0.2–0.6° towards the edge. The coastal (littoral) shelf area is stretched from a coastal line to isobaths of 25–30 m, the central shelf platform lies within isobaths of 30–70 m, and the external shelf (zone of bend) occupies isobaths of 80–105 m (Aibulatov et al. 1981).

In the area of Psou River—Cape Konstantinovsky (14 km south of Khosta) there are relic natural shingle beaches. On the site of fish farm construction near Khosta, in a coastal strip down to depth of 10–12 m, the ground is represented by shingle which is replaced with aleuritic sand at depths of 25–30 m. Deeper 40 m it grades into pelitic (silty) sand. Down to depth of 7 m, the thickness of sand layer under shingle is 2.1–2.8 m, at depths of 11–15 m it increases to 6–8 m, and

Table 6.1 Characteristics of main rivers of the Caucasian coast of the Black Sea (Fashchuk 1998a, b, c)

River	Length, km	Mean runoff, km^3 (min–max)	Watershed area (km^2)	Period of maximal runoff (source of supply)
Rioni	228	12.8 (9–17.3)	13,300	March–May (mixed)
Chorokh	500	8.69 (5–13)	22,000	April–July (precipitation)
Inguri	221	4.63 (0.36–7.75)	4,060	June–July (mixed)
Kodori	84	4.08 (2.73–5.67)	2,030	May (mixed)
Bzyb	–	3.07 (1.94–4.94)	1,410	May (mixed)
Sulsa	–	1.45 (0.93–2.38)	1,100	Evenly (flooding)
Mzmyta	–	1.33 (0.82–2.14)	798	May
All rivers	–	43.2 (34–58.9)	75,000	May

Table 6.2 Mean monthly and annual characteristics of radiation balance on the Black Sea coast near Sochi (Project "The Seas of the USSR" 1991b)

Characteristic	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XI	Annual
Total solar radiation, MJ/m^2	134	201	306	423	603	716	745	670	473	348	197	126	4,942
Albedo, %	26	28	20	20	21	21	21	22	22	23	25	24	22
Radiation balance (*), MJ/m^2	17	33	134	205	318	414	431	343	214	117	33	4	2,263
	59	71	172	230	339	435	452	376	255	167	84	54	2,694
	42	38	38	25	21	21	21	33	41	50	51	50	431

* *Line1* net balance, *Line 2* positive component, *Line 3* negative component

thickness of silts at depths of 80–100 m does not exceed 2–3 m (Lobkovsky et al. 2002).

6.3.2 Climate and Meteorological Conditions

The fish farm is located in wet subtropics, with mild winter (mean air temperature in January is +6°C) and hot summer (mean temperature in July—25–28°C). The characteristics of radiation balance in the region under investigation are presented in Table 6.2.

The geographical position of region and physical–chemical features of coastal waters off Sochi (transparency) determine the fact that at vertical incidence of solar rays only 18% of solar radiation reaching the sea surface penetrate to depth of 10 m (Project "The Seas of the USSR" 1991b).

6.3.2.1 The Wind Regime

The wind regime over the Russian coast of the Black Sea is determined, as over its whole aquatory, by the type of synoptic processes. The features of their intraannual variability specify the prevalence of *northeast winds* on the North Caucasian coast throughout the year and very rare occurrence of north, west and, northwest air flows. On the southeastern coast the *southwest* winds have a maximal occurrence within a year. The northwest and north winds in winter, and southeast winds in summer are observed very rarely.

The coast of Big Sochi is located between these two zones with differently directed air flows, so during the warm season the local breeze circulation—west and southwest (onshore) wind in the daytime and north, northeast (offshore) wind at night—prevails here. Throughout the year the winds of northeastern quarter prevail over the Black Sea aquatory. Their mean annual occurrence is 25–40%; in the northeastern sea it increases up to 40–50% during the winter and autumn months. As a result of offshore winds, the sea level height off the Caucasian coast may vary by 20–30 cm.

The typical winter bora event in the northeastern Black Sea—gusty gale (14–40 m/s) caused by invasions of cold air from the mountains—develops in the

Table 6.3 Mean/maximal duration (hours) of strong winds (>10 m/s) in the Caucasian region of the Black Sea coast (Project "The Seas of the USSR" 1991a)

Month												Year
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
40/96	44/125	34/65	20/49	11/24	7/27	8/13	4/12	4/8	31/55	50/95	31/68	291/637

Table 6.4 Air temperature in ports of the eastern Black Sea by long-term observations (1880–1985) (Project "The Seas of the USSR" 1991b)

Port	T°C	Month												Yearly mean
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
Tuapse	Mean	4.4	5.1	7.4	11.5	16.2	20.2	23.1	23.3	19.4	14.8	10.7	6.9	13.6
	Max	20.0	24.0	29.0	30.0	34.0	36.0	41.0	39.0	38.0	34.0	26.0	24.0	41.0
	Min	−18.0	−19.0	−15.0	−4.0	2.0	7.0	10.0	8.0	2.0	−7.0	−11.0	−18.0	−19.0
Poti	Mean	5.7	6.6	8.9	12.2	16.4	20.3	23.0	23.1	20.2	16.0	11.9	8.1	14.4
	Max	20.0	24.0	33.0	35.0	36.0	39.0	41.0	40.0	36.0	33.0	30.0	22.0	41.0
	Min	−11.0	−11.0	−9.0	−2.0	3.0	8.0	11.0	12.0	6.0	1.0	−5.0	−10.0	−11.0

coastal zone from Anapa to Tuapse. South of this border, in the Sochi area, bora is not observed. The characteristics of wind activity on the Caucasian coast Sea south of Tuapse are presented in Table 6.3.

6.3.2.2 Air Temperature and Humidity

Because of a lack of the long-term data on air temperature and humidity in the area of fish farm installation (Sochi), to characterize intraannual dynamics of these parameters the similar information available for the nearest ports located to the north (Tuapse) and to the south (Poti) of Sochi is used. Interpolation of these data shows that maximal monthly mean temperature (23.2°C) in Sochi is reached in August, and its minimal value (5.0°C) is characteristic of January. But the actual maximum of temperature (41°C) was observed in July, and its minimum (−19°C)—in February (Table 6.4).

In Sochi diurnal mean negative air temperature is usually registered in January—February for 5-8 days, and in December and March—for no more than 2–3 days. With that, over the 100-year period of observations at the Caucasian coast the diurnal mean temperature below −5.0° was registered once every 10–20 years.

Mean monthly air humidity remains almost constant throughout a year (70–80%), with anomalies of 5–7% in winter months.

6.3.2.3 Clouds, Precipitation, Dangerous Weather Events

In the long-term context, by the total amount of clouds (4.3–6.9) the weather in Sochi from May to November is characterized as *semi-clear*. Only in winter

Table 6.5 Mean monthly and annual characteristics of weather events in the Sochi area (Project "The Seas of the USSR" 1991b)

Weather event	Month												Year
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
Total amount of clouds	7.4	7.7	7.5	7.4	6.9	5.6	4.6	4.3	4.7	5.4	6.5	7.2	6.3
Amount of low clouds	5.1	5.0	4.9	4.8	4.1	2.9	2.8	2.6	2.9	3.3	4.1	4.0	3.9
Sunshine duration, h	93	102	134	161	231	271	299	195	236	192	127	90	2,231
Precipitation, mm	156	158	139	102	88	96	93	114	127	114	149	168	1,492
Mean duration of thunderstorms, h	2	2	1	2	5	16	22	29	21	9	6	2	117

months and in March–April it becomes *cloudy*, with cloud amount of 7.2–7.7. With that, because of intensive development of breeze circulation, the amount of low clouds in summer months varies from 2.6 to 2.9, and at transition to the autumn–winter period it increases up to 3.3–5.1. The mean long-term annual sunshine duration is 2,231 h, with its maximum (299 h) in July and minimum (90 h) in December (Table 6.5).

The mean annual amount of precipitation in the Sochi area is 1,492 mm, with their maximum (149–168 mm) in November-February and minimum (88–93 mm) in May–June.

At the Caucasian coast, because of proximity of mountains to the sea, the advective fogs occurring at fog transfer from the sea to land are rarely observed, as this is accompanied with the forced ascending air motion favoring fog dispersion. At the Russian Black Sea coast the mean annual number of days with fog does not exceed 10. For example, in May eleven cases of fogs with total duration of 55 h and maximal event duration of 16.5 h were observed in Sochi during the 1962–1976 period. The maximal occurrence of fogs (14–20%) was noted from 09 p.m. to 06 a.m. at air temperature of 11–14°C.

The intensive ascending motions in the coastal zone of Sochi associated with proximity of mountains to the sea, strengthen the processes of thermal convection and favor occurrence of thermal and air-mass thunderstorms. Their total annual duration is 117 h. These events noted more often in a warm season (up to 35–42 times in a year) have maximal duration (21–29 h) in July, August, and September but can develop in winter months also, lasting 1–5 h.

6.3.3 Waves and Hydrological Conditions

In literary and reference sources there is no information on the state of sea in the investigated area by direct observations of coastal stations. It is possible to judge about wind waves indirectly by the results of theoretical calculations made with the use of synoptic information for a characteristic point in the northeastern Black Sea (44°00′N; 37°00′E.) considered as representative for the whole area, including coastal zone (Table 6.6).

Table 6.6 Characteristics of wind waves in the northeastern Black Sea which are probable once every N years (Project "The Seas of the USSR" 1991a)

Wave characteristic	Period of time	Number of years (N)					
		1	5	10	20	30	50
Mean height (m)	I–III	2.4	2.8	3.1	3.3	3.3	3.4
	IV–VI	1.7	2.0	2.1	2.2	2.2	2.3
	VII–IX	1.6	1.9	2.0	2.1	2.1	2.2
	X–XII	2.2	2.5	2.7	2.8	2.8	2.9
	Year	2.4	2.8	2.9	3.2	3.3	3.9
Mean period (s)	I–III	6.8	7.5	7.8	8.0	8.1	8.3
	IV–VI	6.2	6.7	6.9	7.2	7.3	7.4
	VII–IX	5.9	6.4	6.6	6.7	6.8	6.9
	X–XII	6.9	7.4	7.7	7.9	8.0	8.1
	Year	7.3	8.0	8.2	8.5	8.6	9.4
Wind speed (m/s)	I–III	20.0	23.0	25.0	26.0	27.0	27.0
	IV–VI	14.0	16.0	17.0	17.0	18.0	18.0
	VII–IX	14.0	16.0	17.0	17.0	18.0	18.0
	X–XII	17.0	19.0	20.0	21.0	21.0	21.0
	Year	20.0	23.0	25.0	25.0	25.0	29.0

Practically in all seasons the northeastern region of the Black Sea is characterized by reduced wind activity over its aquatory. The mean annual occurrence of weak winds (<5 m/s) is 63.3%. In April–June it is maximal (77.5%), decreasing to 68.1% in July–September and to 49–57% in winter and spring. During the same seasons the maximal wave height which can reach 2.4 m annually, 2.8 m once every 5 years, up to 3 m once every 10 years, and up to 4 m once in 50 years, is probable.

By the averaged data of long-term (1957–1989) seasonal observations of Southern Research Institute of Fisheries and Oceanography (YugNIRO) at cross-section normal to the coast from Gelendzhik, Sochi, and Sukhumi, along the Caucasian coast of Russia at the 1-mile distance from the coast mean spring sea surface temperature (SST) may vary from 12.98 to 21.35°C, salinity—from 14.79 to 17.77‰, oxygen content—from 5.94 to 7.36 mL/L. In summer the ranges of these parameters are: 21.92–26.90°C, 16.05–17.79‰, and 5.12–6.16 mL/L; in autumn: 11.26–17.53°C, 16.06–18.34‰, and 6.05–6.89 mL/L; and in winter: 7.29–10.05°C, 16.17–18.28‰, and 6.82–8.31 ml/l, respectively. Changes in mean long-term seasonal values of hydrological parameters with depth are presented in Table 6.7.

By data of regular current observations on SST (thermal background) at coast of Big Sochi, in the area of marine fish farm installation, the coldest coastal surface water is observed in February (6.4–7.1°C), and the warmest—in August (26.9–27.0°C). At this, in spring the thermal background at distance of 1 mile from the coast is by 2–3°C higher than directly near the coast (by reason of larger thermal inertia of the sea, as compared with land). In summer these characteristics equalize, and in winter SST at distance of 1 mile from the coast is lower than

Table 6.7 Mean long-term hydrological characteristics of Russian coastal territorial waters in the Black Sea at distance of 1 mile from the coast

Depth, m	Spring			Summer			Autumn			Winter		
	T°C	S‰	O_2, mL/L	T°C	S‰	O_2, mL/L	T°C	S‰	O_2, mL/L	T°C	S‰	O_2, mL/L
0	17.99	16.60	6.75	24.50	17.17	5.57	13.78	17.61	6.48	8.66	17.64	7.34
10	14.98	17.64	6.99	23.62	17.53	5.54	13.97	17.93	6.47	8.55	17.99	7.35
20	11.56	17.92	7.14	20.10	17.79	6.07	13.79	17.99	6.43	8.57	18.10	7.25
30	9.37	18.11	7.20	14.69	18.05	6.73	13.41	18.06	6.41	8.60	18.13	7.20
50	7.68	18.29	6.91	8.58	18.29	6.69	10.81	18.28	6.41	8.25	18.25	7.04

Table 6.8 Mean monthly SST at the Big Sochi coast (Project "The Seas of the USSR" 1991a; Prokopov 1997)

Area	T°C	Month											
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Sochi	Mean	9.5	8.6	8.9	10.9	14.8	19.6	23.7	24.8	22.9	19.2	15.3	11.7
	Max	11.2	10.6	10.4	13.4	18.2	22.5	25.7	26.9	25.8	21.7	17.3	13.3
	Min	7.7	6.4	6.5	8.1	12.3	16.2	20.2	23.1	21.3	16.5	12.8	9.5
Gagra	Mean	10.2	9.2	9.0	10.7	15.0	19.7	23.6	25.0	23.3	19.7	15.7	12.4
	Max	11.8	10.8	10.4	13.4	17.7	23.6	26.5	27.0	25.9	22.0	18.4	14.8
	Min	8.2	7.1	6.8	7.8	12.0	17.3	21.3	23.1	22.1	17.3	12.6	10.3
Pitsunda	Mean	9.8	8.9	9.0	11.4	15.5	20.3	23.7	24.5	23.1	19.4	15.3	12.0
	Max	11.2	9.9	10.4	12.8	17.6	23.1	25.0	26.4	24.3	21.1	17.9	14.5
	Min	8.3	7.6	7.9	9.3	12.9	18.2	22.1	23.0	21.7	17.7	12.9	7.9

Table 6.9 Mean monthly SSS at the Big Sochi coast (Project "The Seas of the USSR" 1991b)

Area	S, ‰	Month											
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Sochi	Mean	16.90	16.65	16.64	16.39	16.00	16.13	16.52	16.82	16.88	16.88	16.92	16.88
	Max	17.63	17.69	17.12	17.44	16.82	16.96	17.20	18.03	17.76	17.74	17.70	17.76
	Min	15.89	15.82	15.62	15.10	15.38	14.89	15.45	15.76	15.97	16.22	15.56	16.14
Gagra	Mean	17.62	17.36	17.20	16.11	15.78	15.88	17.06	17.36	17.66	17.59	17.46	17.43
	Max	18.16	18.02	17.76	16.96	17.88	17.76	18.02	18.42	18.28	18.16	18.08	18.42
	Min	16.19	16.71	16.71	15.52	14.60	14.47	15.65	16.84	17.36	16.84	16.05	15.39

coastal one by 3–5°C, as a result of winter intensification of cyclonic circulation in the eastern open sea, resulting in transport of colder deep water into the convergence zone on its periphery in the coastal area of the sea (Table 6.8).

By data of coastal hydrological observations, in spring minimal sea surface salinity (SSS) in the Big Sochi area practically does not differ from its mean long-term value at distance of 1 mile from the coast (16.60‰). In summer (May, June) minimal salinity at costal stations may be by 2.5–3‰ lower than at distance of 1 mile from the coast because of a greater influence of river runoff. In the autumn–winter period this difference decreases to 1.5–2.0‰ (Table 6.9).

6.3.4 Water Dynamics

The dynamics of coastal Russian territorial waters in the Black Sea is determined by both general features of the sea currents and regional (local) factors—main Black Sea Current synoptic eddies. Along the Caucasian coast of the Black Sea the Main Black Sea Current (MBSC) stream of 40 km width directed to the northwest is located at distance of 15–25 km from the coast (in the Kodori–Bzyb area—at distance of 3–5 km) (Titov 2000). On its coastal periphery the anticyclonic clockwise eddies, well fixed from satellites are regularly generated (Photo 6.4).

The instrumental observations on currents at stationary buoy stations and statistical processing of hydrological time series (Titov et al. 1983; Ovchinnikov et al. 1986; Krivosheya et al. 1997, 2000; Titov 1992, 1993, 2000, 2002, 2005), field investigations (Tkachenko et al. 1992), observations on drifting floats (Zhurbas et al. 2004), and the analysis of satellite images (Zatsepin et al. 2002) allowed to establish and confirm the fact that periodic propagation of anticyclonic synoptic eddies (between the MBSC axis and coast), their traveling into the open sea, active interaction with the cyclonic MBSC gyre and among themselves are the prominent features of water circulation both off the North Caucasian coast and in the whole coastal zone of the Black Sea (Fig. 6.1),

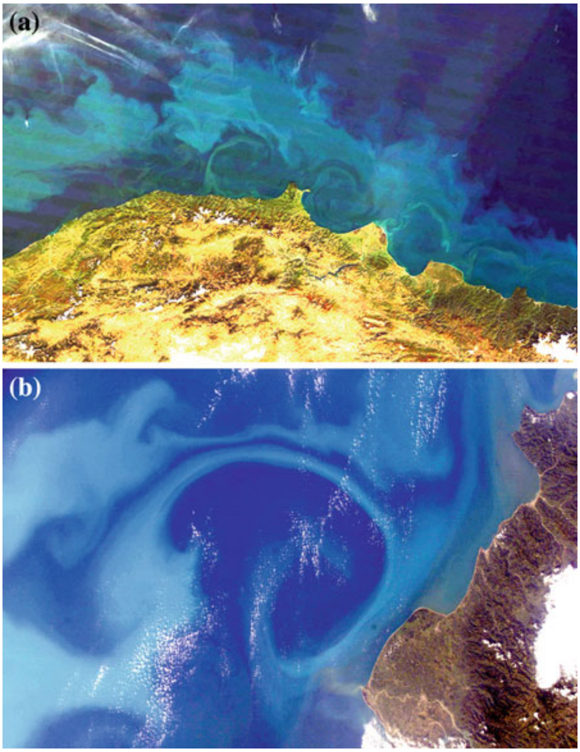

Photo 6.4 The system of anticyclonic synoptic eddies (**a**) and local eddy (**b**) off the Turkish coast in the Cape Sinop area, well fixed from space (Photo from ISS)

Fig. 6.1 The scheme of surface currents in the eastern Black Sea (Tkachenko et al. 1992)

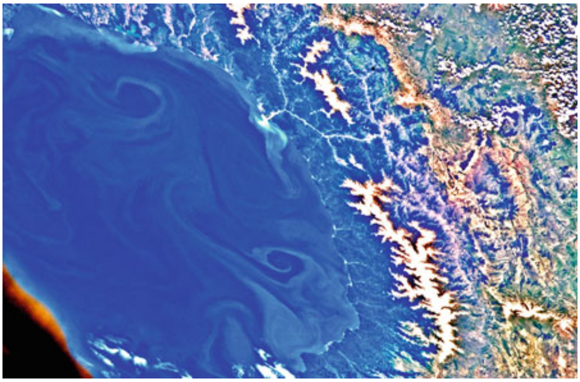

Photo 6.5 Cascade of synoptic eddies along the eastern coast of the Black Sea (Photo from ISS)

With that:

- mean duration of eddy propagation at certain coastal point is 3, maximally 6, days in winter. In summer, they are 5–6 and 12–14 days, respectively, with a maximum of 21 days in May;
- within a month, up to four synoptic eddies cross the area, and for the whole year their number ranges from 19 to 46 (32 eddies, on the average) (Photo 6.5);
- time interval between sequential eddies (period, when costal circulation is mainly determined by the MBSC) is 20–22 days in the winter–spring period and 13–15 days in the spring–summer period;

Table 6.10 Anticyclonic eddies in the northeastern Black Sea (Titov 2002)

Parameter	Statistical characteristic			
	Mean	σ	Max	Min
Distance of center from coast, miles	19	11	60	10
Longitudinal diameter, miles	29	8	50	15
Transversal diameter, miles	20	7	40	10
Thickness, m	265	68	400	160
Total area, km^2	1,620	911	4,308	922
Water volume, km^3	430	183	861	147
Orbital velocity, cm/s	28	5,417	58	10
Volume transport across radial section, m^3/s	380,208	196,148	812,770	160,530

- full turn of drifting float around the synoptic eddy periphery is 1.5–2.5 months, and its horizontal velocity may reach 0.6–0.8 m/s (Zhurbas et al. 2004);
- synoptic eddies in the northeastern Black Sea transport annually from 1,060 to 2,560 km^3 of surface water (1,780 km^3, on the average) (Titov 2002).

Morphometric characteristics of anticyclonic synoptic eddies see in Table 6.10. The consequences of this dynamic water structure are as follows:

- irrespective of season, in the Sochi-Anapa area the coastal currents have reciprocating alongshore character with two diametrically opposite directions (Titov et al. 1983; Ovchinnikov et al. 1986);
- occurrence of flow in the direction of MBSC stream (310°) is 1.5 times higher than in return direction, and the maximal velocities of northwestern currents are 1.5–2 times higher than those of southeastern currents and in some months (October, December) may reach 122–128 cm/s, at monthly mean values of 10–15 cm/s in the period of maxima (winter) (Titov et al. 1983);
- currents of NW sector predominate there from October to April, and southeastern currents—in May and August. In other months the probability of these flow directions is about the same;
- mean annual duration of NW currents is 3.4–5.6 days, maximal—7–8 days in the warm period of year (May–October) and 10–12 days in the cold season (November–April); their minimal duration (2 days) does not change during a year;
- mean annual duration of SE currents is 2.2–6.2 days, maximal—9–10 days in May–October and 3–5 days in November–April; their minimal duration (2 days) does not change throughout a year;
- estimated time of complete water renewal on the shelf of 10 km width at propagation of single synoptic eddy across the certain point, is 35 days (Zatsepin et al. 2002).

6.3.5 Hydrochemical Conditions

The hydrochemical parameters of coastal sea are determined by both intensity of its exchange with open aquatories and volume and quality of river discharge.

Table 6.11 Hydrochemical characteristics (μg-at/L) of Krasnodar and Georgian river offshore zones (Konovalov et al. 1992)

River	Discharge, km^3/year	PO_4		NO_3	NH_4		Si		pH
		0 m	Δ (0–10 m)	0 m	0 m	Δ (0–10 m)	0 m	Δ (0–10 m)	0 m
Rioni	13.00	3.44	0.40	96.0	12.40	10.2	71.6	7.6	7.4
Inguri	5.30	1.65	0.10	13.1	60.20	0.9	34.9	2.4	8.3
Mzmyta	0.80	0.09	–	6.88	1.00	–	34.8	–	8.1
Psou	0.54	0.07	0.00	2.52	0.72	0.2	12.2	1.1	8.2

Table 6.12 Mean long-term hydrochemical characteristics (μg-at/L) of Russian coastal territorial waters in the Black Sea at distance of 1 mile from the coast

Depth, m	Spring		Summer		Autumn		Winter	
	PO_4	SiO_2	PO_4	SiO_2	PO_4	SiO_2	PO_4	SiO_2
0	0.19	17.42	0.24	10.20	0.22	11.45	0.31	20.28
10	0.15	12.51	0.23	9.17	0.23	8.52	0.26	17.96
20	0.18	12.19	0.16	9.07	0.22	11.39	0.27	17.87
30	0.21	13.57	0.17	9.72	0.23	11.86	0.27	18.67
50	0.25	17.42	0.17	11.50	0.17	12.22	0.26	19.33

According to field observations in offshore zones of Krasnodar and Georgian rivers in summer 1989, the content of inorganic phosphorus and nitrogen in the Rioni and Inguri rivers was by a factor of 10–100 higher than in the Psou and Mzmyta rivers (Table 6.11). In the Khosta area in that time the surface concentrations of silicates and nitrates constituted 9.4 and 36 μg-at/L, respectively.

By the averaged data of long-term (1957–1989) seasonal observations of Southern Research Institute of Fisheries and Oceanography (YugNIRO) at cross-section normal to the coast from Gelendzhik, Sochi, and Sukhumi, along the Caucasian coast of Russia at the 1-mile distance from the coast, the mean seasonal concentration of phosphates, for example, changes with depth slightly: from 0.15 to 0.25 μg-at/L in spring, from 0.17 to 0.24-μg at/L in summer, from 0.17 till to 0.23 μg-at/L in autumn, and only in winter the concentration is somewhat higher—0.26–0.31 μg-at/L. The similar vertical homogeneity was noted for silicic acid also (Table 6.12).

6.4 Oil and Chemical Pollution, Sanitary and Epidemiological State of Waters

From the integrated schematic maps of economic activities on aquatory and coast of the Black Sea (Figs. 1.13 and 1.15) follows that its eastern part is characterized by prevalence of NH_4^+ (50–70%) and P_{tot} (34%) loads, and waters off the Georgian coast—by predominance of saturated oilhydrocarbon load (32%). Relative

Table 6.13 Mean (1984–1989) weighted average (0-bottom) content of pollutants (μg/L) in coastal waters of the eastern Black Sea (Fashchuk et al. 1995; Oradovsky et al. 1997; Oradovsky 2002)

Area	Saturated hydrocarbons	Synthetic surfactants	Phenols	Organoclorine pesticides (ng/L)
Anapa	113	31	–	2
Novorossiisk	147	28	Not determined	Not determined
Gelendzhik	142	35	6	4
Tuapse	114	43	6	Not determined
Sochi	142	42	2	Not determined
Pitsunda	57	89	3	4
Sukhumi	203	138	4	–
Poti	160	165	4	8
Batumi	276	229	5	8

weight of N_{tot} and detergents in total loading does not exceed 5–8% there. As compared to data for 1975–1985, by 1989 the concentration of oil hydrocarbons in coastal waters of the eastern Black Sea have increased in ten times and constituted 113–276 μg/L in the whole water column, averaged for the 1986–1989 period. According to observation data of hydrometeorological stations (Fashchuk et al. 1995; Shaporenko 1997), there was an increase in amplitude of fluctuation and mean values of their concentration. For the stated period, the mean values totaled 2–5 MAC (maximum allowable concentration), and the maxima exceeded 30 MAC. Other indicators of water pollution are presented in Table 6.13.

The index of lactose-positive Bacillus coli is one of the indicators of this type of aquatic environment pollution. According to “Methodical instructive regulations on identification of ecological disaster zones” developed at Institute of Geography of the Russian Academy of Sciences in 1992 on the basis of the adopted hygienic classifications (Danilov-Danilyan et al. 1992), ecological situation in water basin is considered as “catastrophic” at the index value (number of Bacillus coli per 1 L of water) exceeding 10^6, “crisis”—at its values from 10^5 to 10^6, and “relatively satisfactory”—at the values less than 10^3.

By the sporadically published data on distribution of this index in the Black Sea waters (Chiburaev 1996), it is known that in 1995 in the area of Novorossisk beaches its value reached 240,000 bacteria/L. During the same time out of 44 water samples taken at four Sochi beaches 6 samples contained from 28,000 to 110,000 Bacillus coli. In Gelendzhik the similar values were fixed in 14 of 54 samples.

The total bacteria, total heterotrophic saprophyte bacteria (HSB), and their ratio are other microbiological indicators of water basin state. According to recommendations of the International Symposium “Ecological modifications and criteria of ecological rationing” (1990), for “catastrophic” situation the value of the first indicator should exceed 10,000 cells/mL, the second—100,000 cells/mL, and the third should be less than 100; for “crisis” situation the corresponding values are 5,000–10,000 cells/mL, 50,000–100,000 cells/mL, and less than 100; and for "relatively satisfactory" they are less than 1,000 cells/mL, less than 5,000 cells/mL, and more than 10^3.

In 1977–1978, during the summer season (peak bacterium development) their total biomass in the Black Sea was 1.5–3 times higher than in the 1951–1967 period, and in 1989 it exceeded the level of 1964 by factor of 5. With that, the production of microorganisms increased by factor of 5–8. It composed 20–60 mg/m^3 in the open sea and 100–200 mg/m^3 per day in the coastal zone. The latter case corresponded to eutrophic waters. In the late 1970s during summer the abundance of bacteria reached 300,000 cells/L in the open sea and 10 million cells/L on the shelf (Sorokin and Avdeev 1991).

By the results of more detailed investigations in summer 1989, the total abundance of bacteria in the 0–20 m layer in the Caucasian coastal zone from Batumi to Anapa ranged from 60,000 to 3,050,000 cells/mL (areas of Novomikhailovka and Batumi–Anakliya, respectively). In the open Black Sea their content exceeded 10^5 cells/mL only in some samples, and at the Bulgarian coast this indicator varied from 80,000 (in offshore zone of Kamchiya river) to 500,000 cells/mL in the Burgas area (Mitskevich et al. 1992).

According to the last-mentioned authors, in the same period the abundance of saprophyte bacteria in coastal waters was close to the upper range of values fixed on the northwestern shelf in the late 1970s. With that, in some cases it exceeded this level by factor of 10–100. Thus, the highest HSB abundance (up to 700,000 cells/mL) was noted at Cape Anakliya (Georgia) and in Burgas Bay (62,000 cells/mL). In the upper 10-m layer it constituted 40,000–60,000 cells/mL in the Adler and Utrish areas and 200–9,000 cells/mL near settlements Golovinka, Gudauta, Novomikhailovka, and in Sudak, Gelendzhik, and Anapa bays.

According to data of Institute of Global Climate and Ecology of the Russian Academy of Sciences, in September, 1992 in coastal waters of the Black Sea from Odessa to Batumi the maximal HSB abundance (0.5–9 million cells/mL) was registered in the Tuapse and Batumi areas. This characteristic varied from tens to hundreds of thousands cells in 1 mL in the northwestern Black Sea and from 5,000 to 50,000 cells/mL along the Crimean coast from Yalta to Kerch Strait.

In summary:

- by index of lactose-positive Bacillus coli in 1995, the situation in the Black sea was characterized as "crisis" (240,000 bacteria/L) in the Novorossiisk area and as close to "crisis" (in several water samples) at beaches of Sochi and Gelendzhik;
- in 1977–1978, during the summer season (peak bacterium development) their total biomass in the Black Sea was 1.5–3 times higher than in the 1951–1967 period, and in 1989 it exceeded the level of 1964 by factor of 5. During the summer period of the late 1970s the abundance of bacteria in the open sea corresponded to "catastrophic" situation (>10,000 cells/mL). The similar situation continued in different coastal areas of the Black Sea, from Bulgaria to Georgia, in the late 1980s;

- by HSB abundance, now the situation is characterized as “catastrophic” on the Georgian beaches (up to 700,000 cells/mL), “crisis” at the Sochi-Adler coast (40,000–60,000 cells/mL), and “relatively satisfactory” in the Sukumi, Gelendzhik, and Anapa areas.

6.5 Assessment of Possible Mariculture Impact on Marine Environment

The analysis of world experience on assessment of marine fish farm impact on environment allows to conclude that their primary role in this context consists in supply of excessive amount of phosphorus and nitrogen compounds, suspended and solid organic substances, as products of fish metabolism and feed residues, to the sea. In the closed (stagnant) basins these factors, undoubtedly, cause adverse consequences for environment. The habitat conditions of aboriginal hydrobiont species get worse as a result of both the change in hydrochemical regime and sea water quality and disturbance of natural biogeochemical processes in bottom sediments.

The analyzed natural mechanisms of accumulation and transformation of pollutants, dissolved and suspended chemical compounds in water and bottom sediments on the Russian Black Sea shelf and numerous results of scientists engaged in studying of water exchange between coastal zone of the northeastern Black Sea and its open aquatory (Eletsky et al. 1994; Neretin et al. 1997; Zatsepin et al. 2002; Shapiro et al. 2002; Krivosheya and Monakhov 2003; Zhurbas et al. 2004; Pykhov 2003; Titov 1992, 2005) convince that, unlike traditional zones of mariculture development in the World Ocean (stagnant fjords of England, Sweden, Denmark), in the North Caucasian costal waters there are powerful natural mechanisms of self-purification. This conclusion is confirmed by the following arguments:

- Surface anticyclonic eddies developing along the coast and propagating in the direction of the MBSC stream are the basic dynamic feature of the area of marine fish farm installation. These eddies actively interact with the stream. In the frontal part of eddy the current is directed from the open sea to coast, and in its rear—in reverse. The current velocities may reach here 70–80 cm/s (sometimes 100–130 cm/s) on the sea surface and 50–60 cm/s (80–100 cm/s) in the shelf bottom layer. As the linear dimensions of surface anticyclonic eddy (50–60 km) exceed shelf width (4–12 km), the “freshening” of shelf with pure water occurs in front of it, while in its rear pollutants are transported into the sea. “Such a strong flow intensively ‘flushes’ the shelf and transports not only polluted waters but also a huge amount of suspended matter into the open sea” (Krivosheya and Monakhov 2003).

- By the results of drifting experiment along the Caucasian coast of the Black Sea (1999) the fact of "absence of a rigid potential barrier between deepwater and shallow zones of the sea" has been established. Floats crossed the shelf edge with "ease," drifting from the coastal zone into the open sea and backward, that indicated the absence of dynamic impediments for transportation of pollutants into the open sea (Zhurbas et al. 2004).
- Satellite monitoring of surface anticyclonic eddies in the Black Sea allowed to fix frequently the detachment of coastal eddy from the coast and its penetration into the open sea. With that, the simultaneous on-board observations registered "a quantity of floating garbage (branches and trees, plastic bottles and bags, canisters, polyfoam pieces, children's toys, etc.) … the impression was given that the vessel operated in the coastal zone rather than in the open sea" (Zatsepin et al. 2002). Thus, propagating synoptic eddies not only accumulate suspensions and water with increased concentrations of fish metabolic products and feed residues but also transport them into the open sea, thereby purifying the fish farm zone.
- By estimation of horizontal water salt balance, it was found that the characteristic time of complete water renewal on the shelf with width of 10 km, as a result of water exchange with the open sea in response to surface synoptic eddy, was about 35 days (Zatsepin et al. 2002). Taking into account the known duration of eddy propagation through a point (up to 6 days in winter and 14 days in summer, at a maximum of 21 days in May), it is easy to calculate that 5–6 eddies in winter and 2–3 eddies in summer provide the complete ventilation of marine fish farm. This seems quite real because on the average four eddies per month are formed there (Titov et al. 1983).
- Mathematical modeling of sedimentary material transport by currents slowly varying (days or weeks) in their direction allowed to conclude that surface anticyclonic eddies in the coastal Russian Black Sea waters with diameter of 30 km and orbital velocity of 25.5 cm/c were capable to transfer up to 2.9×10^5 t of suspension with particle diameter of 7.5 μm (thin aleuritic sand) that exceeded the volume of solid river runoff in this area of the sea by factor of 3. For mean aleuritic sand ($d = 23$ μm) suspension-carrying capacity of eddy decreases to 3.8×10^3 t (only 3% of annual solid river runoff). Moreover, with a decrease in eddy orbital velocity to 17 cm/s, its suspension-carrying capacity becomes 15.5 times lower (Shapiro et al. 2002).
- Features of wind field and its interaction with the Black Sea waters determine intraannual variations in intensity of basin general circulation. In turn, this causes the periodic change in intensity of dynamic upwelling (water lifting in the open sea) and downwelling (water sinking in the coastal zone). As a result, the differently directed seasonal vertical fluctuations of isosurfaces (by seesaw type) are generated between the coastal zone and open sea, leading to the development of intensive lateral horizontal water circulation in this direction

(shelf-open sea). In such a way the periodic self-purification of shelf waters occurs also at seasonal time scale, apart from the contribution of synoptic eddy formations to this process (Neretin et al. 1997; Titov 2005).

6.6 Conclusions

The geographic and ecological information model of the northeastern coast of the Black Sea as mariculture development area includes historical, technological, economic data on this type of economic activity on sea aquatories. The development tendencies in the world and Russian mariculture are investigated. The world experience of engineering solutions at fish farm construction, ecological consequences of their functioning for marine environment, and problems on their control are analyzed. In parallel, the statistical processing of long-term field oceanographic observations (1957–1989) in this area is made. The results of investigations on natural and anthropogenic factors determining supply of organic pollutants and intensity of their biogeochemical transformation, and conditions of sediment accumulation and water ventilation in the Russian Black Sea coastal zone are systematized.

As a result, the priority natural and anthropogenic factors and mechanisms determining the formation of marine environment conditions in the investigated area are identified. The summary Analytical Tables 6.1–6.13 of corresponding physico-geographic, climatic, oceanologic characteristics, and anthropogenic factors allowing users of natural resources not only to plan operatively the technological processes of fish farming (type and volume of feed, feeding regime, selection of farm installation depth, schedule of harvesting, etc.) but to estimate the possible ecological consequences of this economic activity, are compiled.

For example, it is established that along the North Caucasian coast there are the powerful natural mechanisms of marine environment self-purification. The conclusion about almost full ecological safety (in terms of water pollution) of marine underwater fish farm constructed in the Big Sochi area (settlement Hosta) is made.

Moreover, the following is developed:

- practical recommendations on the improvement of farm installation technology (increase in anchor weight and strengthening of ropes capacity) that is associated with necessity to account the periodically high dynamic activity of waters in the area;
- scheme of optimal fish feeding regime (for feed economy), based on the elucidated features of coastal water dynamics (change in current direction and velocity at propagation of eddies) determining periods of calm and high dynamic activity;
- optimal schemes of deepening of fish farm framework, in accordance with seasonal variations of water temperature at different depths and their possible anomalies.

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Chapter 7
Geographic and Ecological Information Model—“Portrait” of the Black Sea Kerch Strait

The great tragedy of the classic of the ancient drama Aeschylus *Prometheus Bound* created at the turn of the VI–V centuries BC tells a touching story of love of the lord of all elements Zeus and daughter of Greek king Inachus beauty Io, maiden of Zeus’ wife Hera. According to myth, to hide dalliance from his jealous spouse, Thunder-Bearer transformed the passion into a white heifer. But Hera was not fooled. She demanded the heifer as a present and charged one hundred-eyed giant Argus to guard the heifer. However, the powerful lord of gods did not like this. He commanded Hermes to kill the guardian that has been done; Hermes cut off the head of Argos by crescent. After this action, eyes of the giant spread all over his body, began to dim, but Hera appeared here with flock of white peacocks, scattered carefully their rests on tails of birds. People say that since then peacocks have such spotted “big-eyed” tails. Hera then forced Io to wander the earth without rest, plagued by a big gadfly to sting her into madness. Escaping from the gadfly, in the mountains of Tauris she met Prometheus chained on the rock. He told her the escapement pathway to Egypt via the Cimmerian Bosporus known now as the Kerch Strait:

> Next, just at the narrow portals of the harbor, you shall reach the Cimmerian isthmus. This you must leave with stout heart and pass through the channel of Maeotis; and ever after among mankind there shall be great mention of you passing, and it shall be called after you the Bosporus.
>
> Translated by H.W. Smyth

In Greek, *Bosporus* means “the passage of the cow”. According to other version of the unknown author lived in the IV century BC, an origin of such name of the Kerch Strait is not so romantic. As it happens, the ancient myths kept a “dossier” of thievish titan Helios, who chose this area of Taurida (from a word “Taurus” that means bull) for his residence and simple hobby. According to the ancient tradition, he owned uncounted herds of bulls, constantly recruiting them by animals stolen at local tribes. One fine day, running from a chase on the back of just stolen bull, Helios has understood that this time he had no chance to escape.

D. Y. Fashchuk, *Marine Ecological Geography*,
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Saving his skin, Helios used his titanic talents and with a subtle movement of the thumb “cut through” the passage separating at that time the Sea of Azov from the Black Sea. Thus, the way for Cimmerian herdsmen pursued a fugitive, has been blocked by the divinely created strait named the Cimmerian Bosporus in honor of successful thief’s operation of the titan. However, this is only one of 200 variants of the Kerch Strait names currently known to the scientists.

Anyhow, but its discoverers, ancient Greeks, believed absolutely fairly that the River Don (Tanais) run into Lake Maeotis (Sea of Azov), and its mouth was located in the northern part of the lake. Historian Herodotus (485–425 BC) called the Sea of Azov with “Mother of Pontus”, believing that it is the sea, but not the Don, that divides possessions of imperial Scythians and Sauromatians, runs into the Black Sea through the Kerch Strait, and gives it a life. Thus, Herodotus considered the Cimmerian Bosporus, or Cimmerian Passage, as a separate geographical object (Sholokhov 2002).

7.1 Geological History

The paleogeographic investigations conducted in the middle of the XX century have proved that the extensive Enikale Strait formed 65 million years ago was the ancestor of the Kerch Strait. It filled the tectonic depression covered the whole present Kerch–Taman region. In the late Miocene–early Pliocene (25–7 million years ago.), in the process of crustal folding and elevation of land the Enikale Strait became much narrower and occupied at that time the territory of Taman Peninsula only. In the late Pliocene (3–2 million years ago), during the continued elevation an archipelago of islands was formed on the premises of the present Taman, and the Enikale Strait ceased to exist, having divided into some smaller straits. The Kerch Strait was one of them (Fig. 7.1).

Only 1–2 million years ago (at the end of Chaudian Epoch) it completely isolated from other straits filled with waters of the ancient Kuban River, and accommodated a water discharge of the Sea of Azov (Blagovolin 1960).

From the current paleogeographic reconstructions of ancient basins of the Black Sea it follows that under the influence of tectonic and climatic factors, and features of water exchange during the Quaternary period (last 1.8 million years) the Black Sea level fluctuated periodically within 20–100 m. As a result, the physico-geographic conditions in the Kerch Strait area changed essentially (see Chap. 3).

In the period of the maximum fall of level (14–12 thousand years ago) the Sea of Azov dried. Its bed represented a coastal lowland plain crossed by the Don valley. The mouth of the river was located by 50 km to the south of the Kerch Strait. During this period the strait itself did not exist. Through a valley located in its place, fresh waters of the ancient Don were discharged into the *New Euxinian* Basin (see Fig. 3.3).

At the final stage of the Black Sea evolution (*Flandrian Basin*) and in the formed Bugaz-Vityaz Sea (10–9 thousand years ago) it reached the present

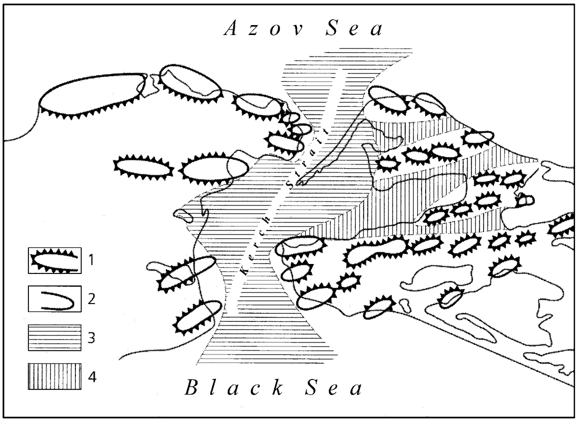


Fig. 7.1 The Kerch–Taman region in the early Chaudian Epoch (3–2 million years ago) (Blagovolin 1960). 1—highlands, 2—areas washed out after the Chaudian Epoch, 3—Kerch Strait; 4—probable position of other straits of the archipelago, dried after the Chaudian Epoch

Photo 7.1 The Kerch Strait acquired its present contours 4–3 thousand years ago in the Jemete Basin period of the New Black Sea Basin of Late Holocene (photo from ISS)

isobaths of 30–35 m. At that time the Kerch Strait represented a shallow bay. Further, with supply of saline water the two-layer H_2S-containing *Kalamitian* reservoir (6–5 thousand years ago) was formed, and in the late Holocene (43 thousand years ago) the level of the new *Jemetin* Sea and ecological conditions in the *New Black Sea* Basin became close to present. The Kerch Strait acquired its present contours (Photo 7.1).

The ideas about the nature of the Sea of Azov and Kerch Strait from the antique epoch to the Middle Ages altered, depending on the change in cultural traditions of ancient inhabitants of their coasts. In the same regard, the names of these two unique geographical objects were also changed. For the historical period, 421 variants of names of the Sea of Azov and 200 variants of names of the Kerch Strait are known (Galkin and Korovin 1990).

Photo 7.2 Chushka Spit (*top*) from the space. Port Krym is at the *left*, Port Kavkaz is on the *spit*, and Tuzla Spit Island is at the *bottom*(photo from ISS)

In the Late Glacial Period (4 thousand years ago) under the influence of short-term (200–300 years) fluctuations of the Black Sea level the processes of abrasion of adjacent coasts of the Kerch and Taman peninsulas became more active. The formation of underwater abrasive platforms has begun in its northern and southern parts. During the Fanagorian regression (2.3 thousand years ago.) and followed Nymphaean transgression (1.8 thousand years) the abrasive material of these platforms was spread over the strait aquatory by currents and served as a basis of accumulative formations (alluvium, or spits) generated at that time and partially existing now (Vise 1927; Nevesskyi 1958).

Ancient Greeks, discoverers of the Kerch Strait, built cities with Temples of Achilles on their tips and gave name "Achilles' run" to the spits themselves. According to the archaeological data and records of Greek geographer and traveller Strabo (64/63 BC to 23/24 AD) (Latyshev 1893), such a city (Porphmion) was located 2,500 years ago on the Crimean side of the strait to the southwest of village Zhukovka, on the already non-existent Enikalian Spit.The similar city-contemporary with the Temple was found on the opposite side of the strait, on the Chushka Spit (Photo 7.2).

Its ancient relict as well as the rests of the still "alive" Kamysh-Burun Spit and "dead" (washed-out) Rubanov and Markitan Spits, were found in the strait in the late 1950s at depths of 7–9 m; their age counts 5–6 thousand years (Fig. 7.2).

During this period the rate of sea transgression altered periodically (see Fig. 3.5). Under its decrease there was a washing-out and disappearance of spits, while an increase in the transgression rate resulted in formation of new and partial recovery of old spits, with their displacement northward or westward from the former position. So, after intensification of transgression (advance) of the Black Sea occurred 1–2 thousand years ago, the relatively young Tuzla Spit was formed in the strait (Photo 7.3).

At present, the strait goes through the next stage of deceleration of the transgression, accompanied here with washing-out and disappearance of accumulative alluvium formations (Boldyrev 1961; Nevesskyi 1958).

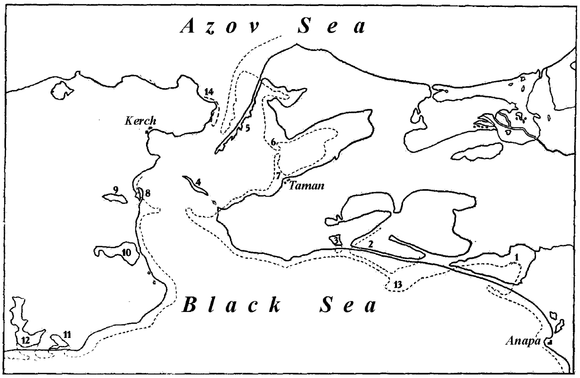


Fig. 7.2 Paleogeographic scheme of the Kerch Strait in the period of the latest Nymphean transgression (Nevesskyi 1958). 1—Vityazevo Liman. 2—Bugaz Liman. 3—Lake Solyonoye. 4—Tuzla Spit. 5—Chushka Spit. 6—Rubanov Spit. 7—Markitanskaya Spit. 8—Kamysh-Burun Spit. 9—Lake Churbashskoye. 10—Lake Tobechikskoye. 11—Lake Koyashskoye. 12—Lake Uzunlarskoye. 13—Mary Magdalene Bank. 14—Yenikale Spit (*Solid line*—present land margins, dashed line—coastline 5–6 thousand years ago)

Photo 7.3 From many accumulative sandy spits formed in the Kerch Strait 2–1 thousand years ago, only the Arshintsevskaya (*left*), Chushka (*top*), and Tuzla Spit (*center*), which became an island in 1925, exist now (photo from ISS)

7.2 Main Transport Corridor of the Azov–Black Sea Basin (History of Exploration and Exploitation)

About 480 BC, notable Miletian Archeanaktus established the first state on the Black Sea coast, which owned the territory from present Feodosiya to Novorossisk, with capital in Panticapaeum (Kerch). During more than 800-year history of its existence and domination over the Black Sea the rulers of the Bosporan Kingdom (the Spartocids dynasty) conducted an active trade with Greece via the Kerch Strait. Only in the middle of the IV century BC the annual export of Bosporan grain in Athens reached 400 medimnos (22,500 tons). Fish was the second item of export.

The sale of Scythian, Sarmatian, and Meotic captive slaves which were shipped mainly to the island of Rhodes, ranked third (Mochulsky 1996).

Apart from grain and fish, wool, corned beef, skins, wine, pottery ware, and ceramic roofing tile were exported to the Mediterranean countries. In turn, textiles, olive oil, wine, metal ware were imported from Athens, Corinth, Rhodes, Thasos, Chios, Kos, and other places. According to Strabo, Panticapaeum, the main port of the Bosporan Kingdom, had docks for 30 sea vessels. In the III–II centuries BC, the sea blockade of King Mithridates by Rome and its subsequent suicide (63 BC) resulted in trade collapse of the Bosporan Kingdom which, nevertheless, existed under the rule of Rome vassals until the Hunnic massacre in the 370s AD (Zubar and Rusyaeva 2004; Kruglikova 1966).

In the X century Kerch (at that time Korchev) was the main trading port in the south of the Kievan Rus. During the Slavic period (more than 200 years), tribute paid to Russian Princes by farmers, hunters, wild-hive beekeepers, and craftsmen, including grain, furs, skins, wool, honey, wax, pottery, cattle, was exported to the Mediterranean. Vegetable oil, wine, ceramics, crockery, and gold ornaments were imported into the power.

Since 1223, after the first invasion of the Mongols into the Crimea, the operations in the port of Kerch were ceased. Only a century later the Tatars offered Genoese to reestablish sea trade and over the next 150 years the Republic of Genoa was provided with food and Slavic captives (labour force) via the Kerch Strait.

In 1475, after occupation of the Genoa colonies in the Crimea by the Turks, the Kerch Strait became the main route of a slave-trade of Turkey. The Crimean Khanate which connected its foreign trade with this country, sold captured Russians, Poles, and Ukrainians as galley-slaves into Turkey.

In the beginning of the XV century the strait became the beaten path for the Zaporizhian Cossacks, by which they returned from their Black Sea campaigns, by-passing Turkish cordons in the Dnieper mouth, across the Sea of Azov, then by the River Molochnaya to the Dnieper, dragging at the final stage their light vessels ("gulls") across the watershed of these rivers. In 1616, the vessels of hetman Konashevych (Sahaidachny) passed this way after taking of Caffa (Feodosiya) by Cossacks and enlargement of captives from Minera and Trebizond.

In 1649, Zaporizhtsi became legitimate, equal right (with the Turks) owners of the Kerch Strait; the rulers of the Ottoman Empire made peace with them, having granted trade concessions and guaranteed navigation safety of Cossack vessels both in the strait and the entire Black Sea, all the way to their entrance into the Mediterranean Sea through the Bosporus. In the following, the marine feats of the Zaporizhian Cossacks were apprised by Russia. At the formation of the Black Sea fleet his Highness Prince Grigory Potyomkin commanded to form its crews "*…from the Cossacks Zaporizhian and peasants of the southern Little Russia as eternally experienced sailors and winners in many marine battles with the enemies*".

In 1774, after signing of the Treaty of Kuchuk Kainarji with the Ottoman Empire, Russia gained the sovereignty over the Kerch Strait, but only in 1821 Alexander I of Russia "*… having recognized as useful to improve our trade in the Black and Azov Searegion…*", opened the trading port of Kerch by its personal decree. During the first 10 years of its existence, the Kerch Strait became a sea link between the Russian Empire and the Caucasian nations of the Circassians and Abazins, and also a transport route for sale of goods and food products from all points of Sea of Azov in Kerch. The Mountaineers were supplied with flour, salt, fish, limestone, chintz, silk, bristle, wax, hemp. In turn, they delivered linen yarn, sawn oak, cheap popular print, oil, felts, knifes, mats, alabaster to Russia by sea route.

As a result, before the beginning of the Crimean War with France, Britain, and Turkey (1854) Kerch from a small settlement (150 houses) with the population of 1,500 people turned into a big trading port city. At the end of the XIX century (1881–1892), 1–3 million poods of grain from the Taman and Crimean Peninsulas, up to 0.5 million poods of timber from Kherson, about 0.4 million poods of fish and black caviar from Akhtarsk and Temryuk were exported annually overseas. Up to 2 million poods of salt from the Arabat Spit were delivered exclusively to the ports of the Baltic Sea. However, the import was inappreciable (100–200 thousand poods) and consisted mainly of coal, tobacco, nuts, and woodwork.

In 1897–1907, up to 1,000 foreign vessels sailed annually through the Kerch Strait. Most of them were Greek and English (on 200–300 vessels), but the flags of Austria, Italy, and Prussia (on 50–100 vessels) were met here also. The total cargo turnover through the strait reached in some years 20 million poods (Mochulsky 1996).

7.3 Distribution of Life

Since the Bosporan Kingdom (IV century BC) and until recently (Volovik et al. 1996) the Cimmerian Bosporus (Kerch trait) was famous for fishery based on the abundant stocks of shad, anchovy, goatfish, sturgeons, and flounders. Poet Polybius wrote about an export of salt fish caught in the Kerch Strait and considered as one of specialty goods in the ancient world. Terrible Roman consul Cato, for example, was indignant that some of his compatriots spent a lot of money, "buying a cask of Pontic salt fish for thirty drachmas…". Strabo, telling about fishing on bonito spawning in the Sea of Azov and then migrating into the Black Sea, noted, however, the large sizes of sturgeons, almost equal to those of dolphins, in the Kerch Strait (Kruglikova 1966). The basis of fish wealth of the Bosporus Cimmerian is made by its food reserves forming here owing to favorable physico-geographic conditions and climate.

7.3.1 Plankton Organisms

7.3.1.1 Phytoplankton

The Black Sea is inhabited by 746 species of algae, subdivided into seven groups. Among them, diatoms and pirophytes have the largest number of species which peak of development is observed in the warm season (Pitsyk 1979). Algae of the Sea of Azov count 361 species relating to six groups. Diatoms, green and blue-green algae, and dinoflagellates are the most numerous of them (Lastivka 1998).

In case of prevalence of current from the Sea of Azov, the phytoplankton concentrations in the Kerch Strait in the Chushka Spit area (Port Krym–Port Kavkaz) coincide with those in the Sea of Azov. The fluctuation range of their spring mean long-term values is 38–1,116 mg/m^3. In summer–autumn, 1996–1997, they reached 1,549–1,641 and 1,360–1,654 mg/m^3, respectively (Studenikina et al. 1998). According to the long-term data, in the summer-autumn season the phytoplankton concentrations in the open Sea of Azov (without the Taganrog Bay) can exceed 2,000 mg/m^3.

Under the steady Black Sea current the phytoplankton biomass in the Kerch strait corresponds to the values observed in the coastal northeastern Black Sea. According to the data obtained by YugNIRO (Project "The Seas of the USSR" The Black Sea 1992), its mean annual value here for the 1960–1988 period was 312 mg/m^3, with fluctuations from 29 (1962) to 1,363 mg/m^3 (1982). The mean seasonal values of this characteristic and its fluctuation range are available only for 1961–1976 (Table 7.1).

According to the data of field investigations conducted by YugNIRO Laboratory of Marine Ecosystem Protection, in the near-strait area in winter 1998 the phytoplankton biomass amounted to 219 mg/m^3; in summer and autumn 1999, 84 and 552 mg/m^3, respectively; and in winter and spring 2000, this characteristic reached here 137 and 175 mg/m^3. By the materials of winter survey (19 stations) of the southern Kerch Strait (between Cape Kamysh-Burun from the Crimean side and Cape Tuzla from the Caucasian side), conducted by specialists of the same laboratory on December 14–15, 1999, under the Black Sea current the weighted average biomass of phytoplankton in the layer of 0 m-bottom varied from 182 to 560 mg/m^3, with mean value of 328 mg/m^3. According to the results of survey carried out in the same area on December 5, 2000 (16 stations) also at south winds, the phytoplankton concentrations ranged from 32 to 243 mg/m^3, with the mean value of 76 mg/m^3.

The values obtained fall in the range of the long-term mean seasonal values for the coastal zone of the eastern Black Sea. The latter (Table 7.1), thus, can be used for an estimation of damage of phytoplankton population due to economic activities on the Kerch Strait aquatory in conditions of prevalence of the Black Sea currents here.

Table 7.1 Phytoplankton biomass (mg/m^3) in the 0–25 m layer in the eastern Black Sea, 1961–1976 (Mashtakova and Roukhijainen 1979)

Biomass	Months				
	II–III	V	VI	VII	VIII
Mean	403	103	87	147	90
Range	17–3,782	21–237	19–344	39–504	12–240

7.3.1.2 Zooplankton

The composition of Black Sea zooplankton counts about 120 species of organisms and about 20 species of larvae of bottom invertebrates (Sorokin 1982). Among them, 60% of species are of the Mediterranean origin, and the fodder forms are represented by copepods, cladocerans, chaetognaths, and larvaceans. The zooplanktonic community of the Sea of Azov includes 150 species of animals, from which 94 species are characteristic of the open sea, and 74 species are met most often. Among them, infusorians, rotifers, copepods, cladocerans, and polychaetes are prevalent (Mirzoyan 2000).

In periods when the Azov current prevails, the concentrations of fodder zooplankton in the southern Kerch Strait correspond to those in the Sea of Azov, which mean annual values in 1985–2000 amounted to 125 mg/m^3, ranged from 24 to 294 mg/m^3 that was four times larger than in the strait (Budnichenko and Chashchina 2000). Moreover, the mean values of this characteristic vary considerably with a season of the year (Table 7.2). For example, in spring 1996–1997 they amounted to 1,060 and 174 mg/m^3; in summer, 388 and 750 mg/m^3; and in autumn, 204 and 164 mg/m^3 (Studenikina et al. 1998). Thus, advection of Azov Sea water into the strait and Black Sea favors an enrichment of forage base of these areas all the way to Feodosiya and Sudak and formation of the centers of zooplankton and fish juvenile concentration here during the summer period.

In situations when the Black Sea current prevails in the strait (south winds), Black sea waters penetrate here. The concentrations of fodder zooplankton in these waters differ several times from those in the Sea of Azov. The mean long-term value of this characteristic in the eastern Black Sea for the 1959–1988 period was 75 mg/m^3, ranging from 27 to 161 mg/m^3 (Project "The Seas of the USSR" The Black Sea 1992).

The character of seasonal variations in zooplankton biomass in the coastal zone of the northeastern Black Sea (Feodosiya-Novorossisk) was estimated for the period of 1959–1974 only (Table 7.3). These values differ essentially from the mean long-term values for the sea and require updating by the latest data. Such data were obtained as a result of hydrobiological surveys in the near-strait area, conducted by specialists from YugNIRO Laboratory of Marine Ecosystem Protection. In winters 1998, 1999, and 2000 the fodder zooplankton biomass in this area amounted to 6.7; 18.5 and 15.5 mg/m^3, respectively; in summer 1999, this characteristic did not exceed 2.8 mg/m^3; and in spring 2000, it was 10.3 mg/m^3.

Table 7.2 Seasonal variations in fodder zooplankton biomass (mg/m^3) in the Sea of Azov in 1985–2000 (Budnichenko and Chashchina 2000) and 1988–1998 (Mirzoyan 2000)

Biomass	Months						
	IV	V	VI	VII	VIII	IX–X	Average
Mean	121, 158[a]	637[a]	379[a], 383	39[a], 155	10[a], 34	25, 28[a]	125, 207[a]
Range	3–283		24–1,184	17–663	3–207	1–88	24–294

[a] According to Mirzoyan's data

Table 7.3 Seasonal variations in fodder zooplankton biomass (mg/m^3) in the coastal zone of the northeastern Black Sea during the 1959–1974 period (Greze and Fedorina 1979)

Area	Months					
	II–III	V	VI	VII	VIII–X	Mean
Feodosiya	225	339	448	363	301	335
Novorossisk	243	354	511	329	310	349
Average	234	346	480	346	305	342

The similar investigations carried out in the southern Kerch Strait on December 14–15, 1999 and December 5, 2000 under south winds, allowed to register in the strait (between Cape Kamysh–Burun and Cape Tuzla) the average fodder zooplankton concentrations of 31 and 23 mg/m^3, respectively, with variations between stations from 20.1 to 51.9 mg/m^3 that was much lower, compared to mean long-term data for the coastal area from Feodosiya to Novorossisk for 1959–1974 but well corresponded to the mean long-term data for the coastal zone of whole eastern Black Sea (Project "The Seas of the USSR" The Black Sea 1992). Thus, when estimating a possible damage for zooplankton population in the Kerch Strait due to economic activities on its aquatory in the periods of the Black Sea current development, the mean long-term values for the eastern sea, making 16–161 mg/m^3 (75 mg/m^3 on the average), can be taken as the initial concentrations.

7.3.1.3 Ichthyoplankton

Being the passive life forms, eggs of pelagic fish and mollusk species, and fish larvae (ichthyoplanktonic organisms) penetrate into the Kerch Straut zone with the prevailing currents.

About 20 fish species constantly live and spawn in the Sea of Azov (Nadolinsky 2000). Among them, Azov kilka and anchovy are the predominant summer-spawning species. Mass spawning of kilka occurs in late May–early June in the eastern sea and adjacent central part of the Taganrog Bay. Thus, at early stages of development this species almost is not met in the Kerch Strait.

Penetration of ctenophore into the Sea of Azov in recent years resulted in a sharp decrease in concentration of anchovy eggs and larvae in its southern (near-strait) part and the strait zone, and now their main mass started to concentrate in the western sea, where ctenophore penetrates only in August. The mass spreading of ichthyoplankton from this area of the Sea of Azov into the Kerch Strait under the influence of north winds is unlikely.

During the 1986–1992 period eggs of 27 fish species and larvae of 43 fish species were registered in the Black Sea. Among them, eggs of 16 species and larvae of 18 species were found in the northern sea (Crimean coast). The egg concentrations of the most widespread species, such as anchovy, scad, and whiting, in the coastal zone of Crimea ranged from a few to several tens of eggs per square meter (Gordina and Klimova 1995).

7.3.2 Benthic Organisms

In 1934, the first investigators of bottom biocenoces of the Kerch Strait have defined here nine communities of organisms (Vorobyov 1934): (1) *Cerastoderma (Cardium)–Ampelisca–Corophium.* (2) *Mytilus–Mytilaster–Balanus improvisus.* (3) *Cardium edule–Policheta.* (4) *Mytilus–Ascidiella.* (5) *Venus gallina–Tapes rugatus–Cardium edule.* (6) *Modiolus adriatica–Meretrix rudis–Ascidiella.* (7) *Ostrea taurica.* (8) *Ostrea sublamellosa.* (9) *Burnea candida* (Fig. 7.3a).

In 20 years the essential changes in structure of bottom organism communities were fixed in the strait: reduction (up to the complete disappearance) or expansion of some biocenoses and appearance of new ones (Nesis 1957). So, the area of biocenosis of mussels *Mytilus–Mytilaster–Balanus improvisus* reduced considerably due to the intensive development of *Cerastoderma (Cardium)* biocenosis. The *Mytilus–Ascidiella* biocenosis and the most of *Cardium edule–Policheta* biocenosis disappeared. They were replaced with the *Nephthys–Oligocheta* biocenosis (Fig. 7.3b). The researchers considered salinization of the sea due to regulation of the Don River runoff as the main cause of the observed changes.

In 1986, 71 species of benthic organisms were found in the bottom community of the Kerch Strait (Litvinenko et al. 2001). They included: 28 species of mollusks (22 species of bivalves, 5 species of gastropods, and 1 chiton species), 21 species of polychaetes, 3 ascidian species, 2 sea anemone species, 13 species of crustaceans, 1 species of nemertean worms, 3 species of echinoderms. The share of dominating bivalves in species composition, abundance, and total biomass of zoobenthos community amounted to 31, 59 and 86.3%, respectively, with the mean zoobenthos biomass of 431 g/m^2 and abundance of 386 inds./m^2 (Fig. 7.4).

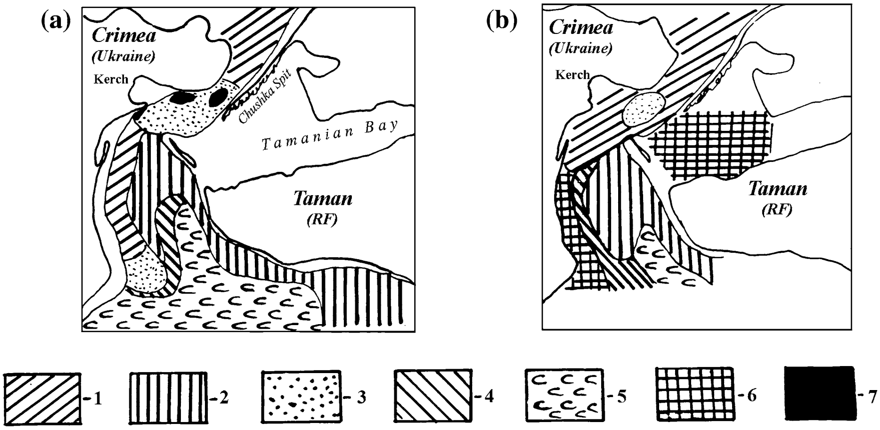
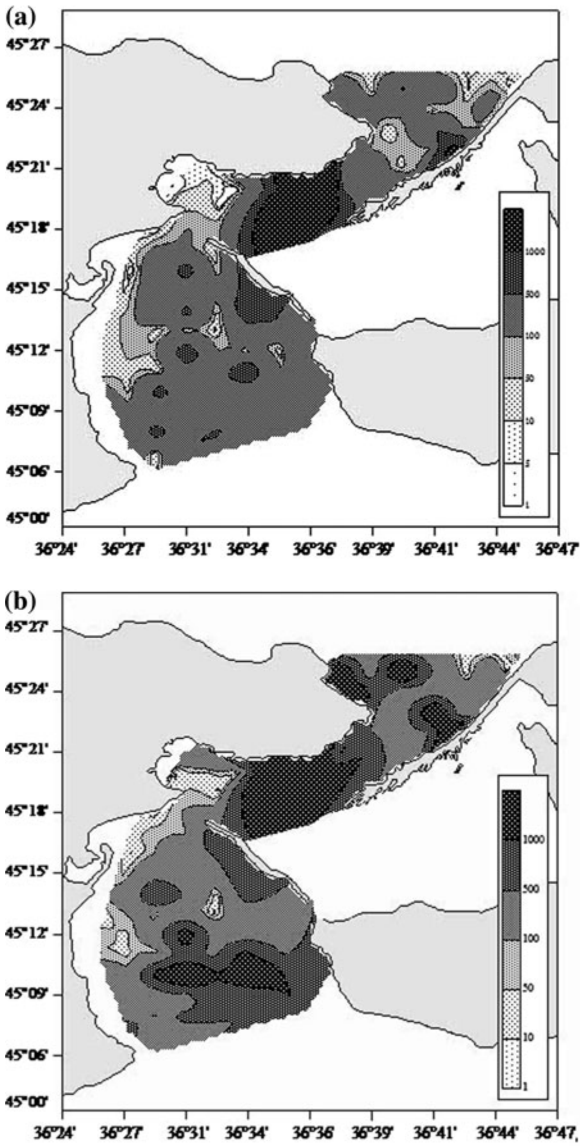


Fig. 7.3 Biocenoses of the Kerch Strait in 1933–1934 **a** (Vorobyov 1934) **b** (Nesis, 1957). (1—*Cerastoderma* (*Cardium*); 2—*Venus* (*Chamelea*); 3—*Mytilus*; 4—*Modiolus*; 5—*Ostrea*; 6—*Nephthys*; 7—commercial concentrations of mussels)

Fig. 7.4 Total biomass, g/m^2 (*top*) and abundance, inds./m^2, (*bottom*) of zoobenthos in the Kerch Strait in June 1986



Sestonophages predominated in the trophic structure of bottom community. Their shares in species composition, abundance, and total biomass of zoobenthos were 35, 59.8, and 91.1%, respectively. Mollusks prevailed in species composition (63.7% of abundance and 88% of total zoobenthos biomass), with domination of bivalves, 92.7% of abundance and 97.5% of total biomass. Polychaetes also had rather high values of the above characteristics. Their mean abundance reached 137.2 inds./m^2, or 32% of total zoobenthos abundance. The biomass of this group of animals equaled 21.5 g/m^2, or 5.5% of total biomass of zoobenthos.

Photo 7.4 Bivalve mollusk *Cerastoderma glaucum (Cardium)* or "cockle", Mediterranean species, very persistent to salinity decrease (from 35 to 10–12%), in the Kerch Strait prefers shallow waters of the Crimean coast with silt or sandy bottom and high current velocities

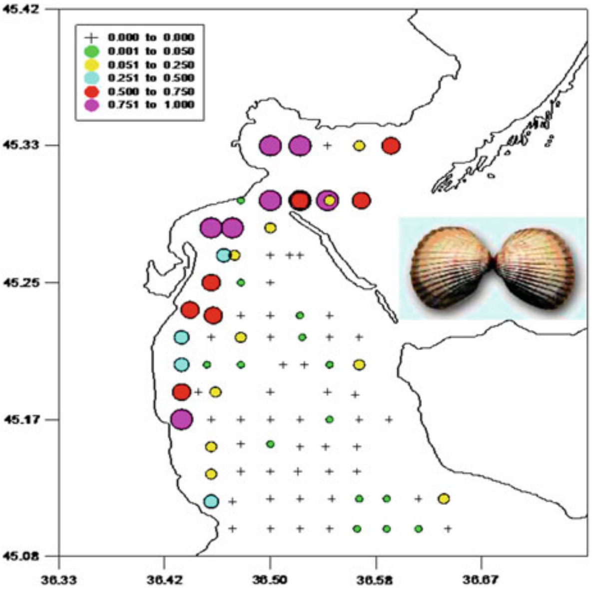


Fig. 7.5 Distribution of biomass (g/m^2) of mollusk *Cerastoderma glaucum* in the Kerch Strait in 1986 (Figure by N. Kucheruk)

Along the western coast of the strait the *Cerestoderma glaucum* biocenosis including 26 species of organisms is located (Photo 7.4, Table 7.4, Fig. 7.5). The mean biomass of animals in this biocenosis reaches on the average 310.6 g/m^2, ranging from 22 to 1,208.4 g/m^2. The biomass of dominating species is on the average 80.1% (from 53 to 98%). The community consisting of 13 species of benthic organisms is distinguished in this biocenosis, in which, along with *Cerastoderma glaucum* (58% of biomass), mollusk *Polititapes aurea* is present as the second-order dominant (21% of biomass).

The central and western parts of the strait south of the Tuzla Spit Island are occupied by the community of mollusk *Chamelea gallina* (Photo 7.5) including its

Table 7.4 Characteristics of species in *Cerastoderma glaucum* biocenosis in 1986 by N. Kucheruk

Species		Occurence (%)	Biomass (g/m^2)			Biomass share (%)		
			Average	min	max	Average	min	max
1.	*Cerastoderma glaucum*	100	310.6	22.00	1,208.40	80.1	53.73	98.03
2.	*Polititapes aurea*	23	6.769	0	48.000	4.9	0.00	35.82
3.	*Melinna palmata*	100	7.314	0.120	56.000	3.0	0.06	18.68
4.	*Chamelea gallina*	62	4.692	0	22.400	2.4	0.00	11.53
5.	*Callianassa pestai*	23	6.123	0	37.200	2.3	0.00	23.74
6.	*Cunearca cornea*	23	5.138	0	26.000	2.0	0.00	17.03
7.	*Macropipus depurator*	8	1.323	0	17.200	1.5	0.00	20.12
8.	*Nana donovani*	77	3.563	0	13.680	0.9	0.00	3.62
9.	*Nephthys hombergii*	77	0.898	0	4.800	0.5	0.00	3.23
10.	*Abra nitida*	46	0.738	0	4.800	0.5	0.00	3.41
11.	*Actinia equina*	15	0.431	0	4.000	0.4	0.00	2.84
12.	*Acanthocardia tuberculata*	8	0.523	0	6.800	0.4	0.00	4.57
13.	*Actinothoë clavata*	8	0.308	0	4.000	0.2	0.00	2.84
14.	*Pitar rudis*	8	0.308	0	4.000	0.2	0.00	2.69
15.	*Balanus improvisus*	8	0.046	0	0.600	0.2	0.00	2.57
16.	*Eriphia verrucosa*	8	0.523	0	6.800	0.2	0.00	2.27
17.	*Nereis succinea*	23	0.554	0	3.600	0.1	0.00	1.09
18.	*Diogenes pugilator*	15	0.123	0	1.000	0.1	0.00	0.51
19.	*Ctenicella appendiculata*	8	0.338	0	4.400	0.1	0.00	0.80
20.	*Nerinides tridentata*	15	0.092	0	0.800	0.0	0.00	0.27
21.	*Brachynotus sexdentatus*	8	0.092	0	1.200	0.0	0.00	0.40
22.	*Mytilaster lineatus*	15	0.077	0	0.600	0.0	0.00	0.13
23.	*Nereis fucata*	8	0.215	0	2.800	0.0	0.00	0.23
24.	*Tritia reticulata*	8	0.185	0	2.400	0.0	0.00	0.22
25.	*Nereis zonata*	8	0.185	0	2.400	0.0	0.00	0.19
26.	*Pectinaria koreni*	8	0.025	0	0.320	0.0	0.00	0.11

biocenosis (32 species), with the mollusk share in total biomass of 70–90% (Table 7.5), and four communities with the second-order dominants, such as *Cerastoderma glaucum* (23–46%), *Melinna palmata* (23–43%), *Pitar rudis* (25–37%), *Flexopecten ponticus* (20–30%) (Fig. 7.6).

The southwestern part of the Kerch Strait is occupied by biocenosis of bivalve mollusk *Modiolus adriaticu* (Fig. 7.7), including 41 species of bottom organisms (Table 7.6). The average biomass of animals in the biocenosis amounted to 201 g/m^2, with range of 42–528 g/m^2. The biomass of predominant species averages 51% (from 31 to 74%). In this biocenosis the community consisting of 13 species of benthic organisms is distinguished, in which, along with *Modiolus adriaticu* constituting 37% by biomass, mollusk *Polititapes aurea* is present as a second-order dominant (21% of biomass).

Photo 7.5 Bivalve mollusk *Chamelea (Venus) gallina* is a Mediterranean species inhabiting bottom sites of the Kerch Strait with sandy and mud-sandy grounds (venus sands) in the depth range of 5–20 m

In the northern part of the Kerch Strait the reciprocating character of water exchange with the Sea of Azov provides an intensive ventilation of the near-bottom layer, export of polluting substances outside its aquatory, and constant nutrient replenishment, determining thereby the existence until recently of extensive biocenosis of mollusks (*Mytilus galloprovincialis*) between the Chushka Spit and Kerch Peninsula (Photo 7.6). However, since the mid-1970s the degradation of mussel population has been observed here. From the early 1950s to the mid-1960s their stock reduced from 100,000 to 50,000 t. In 1979, it was 15,000 t, and in 1989, only 2,000 t. In this period the stock of mussels in the near-strait zone decreased from 300 to 78,000 t. In the late 1980s the harvesting of mussels in this area was ceased (Fashchuk et al. 1991). Now the local mussel biocenosis is located in the northern part of the strait, nearby the navigational channel. The mollusk biomass reaches here 5.2 kg/m^2, with maximum of more than 10 kg/m^2 and size of 23–72 mm. The total stock of mussels is estimated in 3,800 t, and commercial stock, in 3,100 t.

The community of mollusk *Cunearca cornea*, an invader from the Black Sea, located in the coastal zone is the second-largest bottom biocenosis in this area. Its mean abundance was 1,320 inds./m^2, and biomass, 444 g/m^2.

In the late 1940s mollusk *Rapana thomasiana thomasiana Grosse* (rapa whelk) was brought into the Black Sea. In the second half of the XX century it widely distributed over the Black Sea shelf, occupied the Kerch Strait and even penetrated into the southern Sea of Azov (Photo 7.7). By estimations made in 1977–1984, the concentration density of large individuals (more than 93 mm) of new invader in the strait increased by a factor of 3.6–5.5 times, as compared with 1965. Its mean density reached here 7 individuals per 100 m^2, with a maximum of 10 individuals per 100 m^2 (in the northern part of the strait on Bank Tserkovnaya, where the maximum mussel concentration of 1 kg/m^2 was observed). Their stock at that time

Table 7.5 Characteristics of species in *Chamemea gallina* biocenosis in 1986 by N. Kucheruk

Species	Occurence (%)	Biomass (g/m^2)			Biomass share (%)		
		Average	min	max	Average	min	max
1. *Chamelea gallina*	100.0	137.78	12.00	370.80	69.0	49.3	90.3
2. *Tritia reticulata*	81.8	8.29	0	32.80	5.4	0	18.7
3. *Pitar rudis*	81.8	10.09	0	24.00	4.5	0	10.2
4. *Polititapes aurea*	45.5	7.38	0	30.40	3.1	0	11.5
5. *Modiolus adriaticus*	27.3	4.69	0	22.00	2.5	0	12.6
6. *Melinna palmata*	54.5	3.66	0	11.20	1.6	0	4.8
7. *Cerastoderma glaucum*	27.3	2.58	0	14.00	1.3	0	6.0
8. *Gastrana fragilis*	9.1	3.27	0	36.00	1.2	0	13.5
9. *Acanthocardia paucicostata*	36.4	3.02	0	13.60	1.2	0	6.9
10. *Terebellides stroemi*	9.1	0.22	0	2.40	1.1	0	12.5
11. *Cunearca cornea*	18.2	2.18	0	14.00	1.0	0	6.5
12. *Abra nitida*	63.6	1.16	0	4.80	1.0	0	4.2
13. *Actinia equina*	72.7	3.19	0	14.00	1.0	0	3.4
14. *Ctenicella appendiculata*	27.3	1.82	0	8.00	0.9	0	4.0
15. *Acanthocardia tuberculata*	9.1	0.64	0	7.00	0.7	0	8.2
16. *Spisula subtruncata*	36.4	1.91	0	14.00	0.7	0	4.7
17. *Pectinaria koreni*	36.4	1.61	0	10.00	0.6	0	3.8
18. *Callianassa pestai*	18.2	1.35	0	10.00	0.5	0	3.4
19. *Crangon crangon*	18.2	1.09	0	8.00	0.5	0	4.0
20. *Calyptraea chinensis*	36.4	0.95	0	5.60	0.5	0	3.2
21. *Gouldia minima*	18.2	0.11	0	0.80	0.4	0	4.2
22. *Mytilaster lineatus*	45.5	0.51	0	2.40	0.3	0	1.4
23. *Diogenes pugilator*	45.5	0.49	0	2.80	0.2	0	0.9
24. *Synisoma capito*	9.1	0.04	0	0.40	0.2	0	2.1
25. *Leiochone clypeata*	36.4	0.36	0	3.20	0.2	0	1.4
26. *Spisula triangula*	9.1	0.22	0	2.40	0.1	0	1.5
27. *Nephthys hombergii*	54.5	0.22	0	0.60	0.1	0	0.3
28. *Brachynotus sexdentatus*	9.1	0.36	0	4.00	0.1	0	0.9
29. *Nerinides tridentata*	18.2	0.08	0	0.60	0.1	0	0.7
30. *Nana donovani*	9.1	0.05	0	0.60	0.0	0	0.3
31. *Glicera tridactyla*	9.1	0.02	0	0.20	0.0	0	0.1
32. *Spio filicornis*	9.1	0.01	0	0.08	0.0	0	0.0

amounted to 1.2–1.92,000 t, with the mean mollusk weight of 234 g. The possible commercial harvesting of rapa whelk without damage to its population is estimated in 120 t/year (Rubinshtein and Khizhnyak 1988).

The coastal zone (depths of 1–3 m) of the southern Chushka Spit (north mouth of the strait) is occupied by broadleaved Zostera (*Zostera marina*). Its concentrations here vary from 20 to 300 g/m^2, and the total stock is 800 t (Photo 7.8).

The biocenosis of mytilaster is located in the northern part of the area nearby the navigational channel. The mean abundance of mollusks in it is 1,000 inds./m^2, and their biomass, 291 g/m^2.

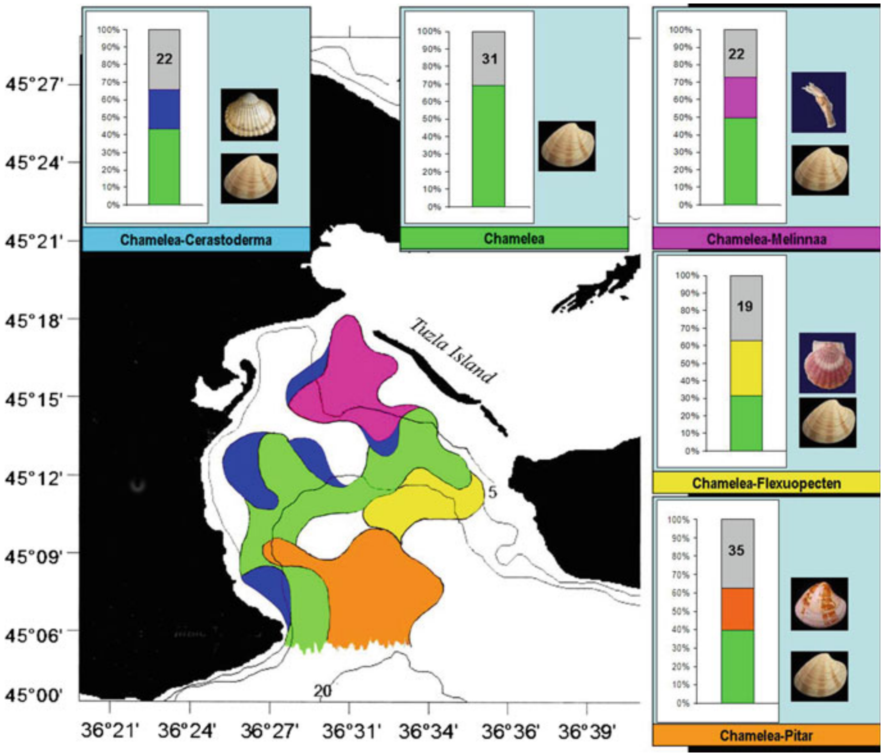


Fig. 7.6 Community of mollusk *Chamelea gallina* in the Kerch strait in June 1986. Communities: *green—Chamelea; blue—Chamelea-Cerastoderma; violet—Chamelea-Mellina; orange—Chamelea-Pitar; yellow—Chamelea–Flexopecten.* Diagrams show shares (by biomass) of dominant species in communities. Numbers on diagrams—other species quantity by Fashchuk and Kucheruk

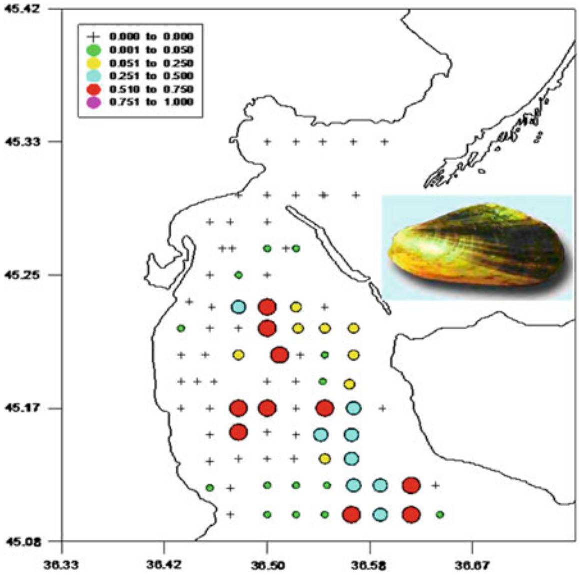


Fig. 7.7 Distribution of mollusk *Modiolus adriaticus* biomass (g/m^2) in the Kerch Strait in June 1986 by N. Kucheruk

Table 7.6 Characteristics of species in *Modiolus adriaticus* biocenosis in 1986 by N. Kucheruk

Species	Occurence (%)	Biomass (g/m^2)			Biomass (%)		
		Average	min	max	Average	min	max
1. *Modiolus adriaticus*	100.0	200.889	42.00	628.000	50.8	30.7	74.4
2. *Polititapes aurea*	83.3	44.022	0	108.000	11.7	0	34.8
3. *Pitar rudis*	83.3	24.516	0	108.000	6.9	0	17.6
4. *Flexopecten ponticus*	66.7	22.667	0	100.000	6.5	0	33.2
5. *Chamelea gallina*	66.7	20.378	0	86.000	5.0	0	19.3
6. *Ascidiella aspersa*	22.2	13.644	0	120.800	4.0	0	35.2
7. *Tritia reticulata*	83.3	9.422	0	42.000	2.7	0	7.5
8. *Mytilaster lineatus*	72.2	13.538	0	102.000	2.6	0	18.2
9. *Terebellides stroemi*	72.2	6.600	0	26.400	2.1	0	7.8
10. *Macropipus holsatus*	5.6	1.978	0	35.600	1.5	0	27.2
11. *Gastrana fragilis*	44.4	5.622	0	32.000	1.4	0	10.9
12. *Melinna palmata*	22.2	9.549	0	160.000	0.9	0	13.8
13. *Callianassa pestai*	16.7	2.178	0	20.000	0.6	0	4.6
14. *Ostrea edulis*	5.6	1.133	0	20.400	0.6	0	10.0
15. *Abra nitida*	61.1	1.667	0	12.000	0.5	0	2.7
16. *Gouldia minima*	55.6	1.231	0	3.600	0.5	0	2.8
17. *Calyptraea chinensis*	72.2	1.031	0	8.600	0.4	0	3.1
18. *Gibbula albida*	5.6	0.667	0	12.000	0.3	0	5.9
19. *Pectinaria koreni*	55.6	1.056	0	6.000	0.3	0	1.4
20. *Cerastoderma glaucum*	33.3	0.676	0	6.000	0.2	0	2.3
21. *Nereis succinea*	11.1	0.422	0	4.800	0.1	0	1.4
22. *Nephthys hombergii*	50.0	0.309	0	1.600	0.1	0	0.5
23. *Perinereis cultrifera*	5.6	0.222	0	4.000	0.1	0	1.4
24. *Diogenes pugilator*	22.2	0.222	0	1.200	0.1	0	0.4
25. *Hippolyte longirostris*	5.6	0.059	0	1.000	0.0	0	0.8
26. *Lepidohitona cinerea*	11.1	0.089	0	0.800	0.0	0	0.6
27. *Glicera tridactyla*	22.2	0.127	0	1.200	0.0	0	0.4
28. *Amphiura steponovi*	27.8	0.122	0	0.800	0.0	0	0.3
29. *Mytilus galloprovincialis*	5.6	0.156	0	2.800	0.0	0	0.5
30. *Nereis longissima*	11.1	0.071	0	0.800	0.0	0	0.2
31. *Macropipus depurator*	5.6	0.022	0	0.400	0.0	0	0.2
32. *Actinia equina*	11.1	0.071	0	1.200	0.0	0	0.2
33. *Hiatella rugosa*	5.6	0.067	0	1.200	0.0	0	0.2
34. *Ctenicella appendiculata*	5.6	0.044	0	0.800	0.0	0	0.1
35. *Amphitrite gracilis*	5.6	0.022	0	0.400	0.0	0	0.1
36. *Nereis rava*	11.1	0.013	0	0.200	0.0	0	0.1
37. *Leiochone clypeata*	11.1	0.016	0	0.200	0.0	0	0.0
38. *Harmothoë imbricata*	5.6	0.007	0	0.120	0.0	0	0.0
39. *Phyllodoce lineata*	5.6	0.011	0	0.200	0.0	0	0.0
40. *Myriochele heeri*	5.6	0.004	0	0.080	0.0	0	0.0
41. *Osterenia thomsoni*	5.6	0.002	0	0.040	0.0	0	0.0

Photo 7.6 Bivalve mollusk *Mytilus galloprovincialis* in the Kerch Strait inhabits all types of grounds, except for shell limestone, is persistent to sharp changes of water temperature (eurythermic) and very low concentrations of dissolved oxygen (euryoxibiont) and is up to temporary (up to 30 days) anaerobiosis

Photo 7.7 Mollusks *Cunearca cornea* and *Rapana* befor cooking (photo by author)

The central part of the strait (close to the navigation channel) is inhabited by community of Nereis, including five species of animals: polychaetes Nereis succinea (40 inds./m^2; 32 g/m^2), barnacles Balanus improvisus (160 inds./m^2; 14 g/m^2) (Photo 7.9), anemones Actinothoe clavata (40 inds./m^2; 5.6 g/m^2), and polychaetes Nephthys hombergii (120 inds./m^2; 5.2 g/m^2).

Among all species of zoobenthos found in the Kerch Strait, forage organisms are represented by all polychaetes and mollusks with size of less than 25 mm. The mean total biomass was 239 g/m^2, and estimated annual production, 650 g/m^2 or 20,371 t.

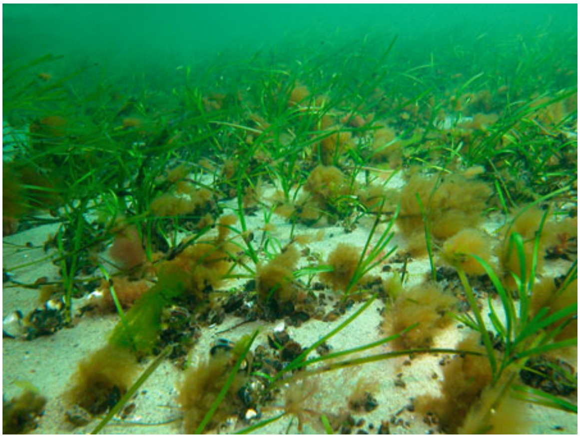


Photo 7.8 Eelgrass *Zostera marina* is a typical representative for bottom landscapes of the central part of the Kerch Strait between the Tuzla and Chushka Spits (www.algasebase.org)

Photo 7.9 Barnacles *Balanus improvisus*

7.3.3 Fishery Characteristic of the Strait

The main fish species met in the Kerch Strait zone permanently or periodically include: goby (16 species in the Sea of Azov), Azov shad, Black Sea shad, striped mullet, golden mullet, small scad, goatfish, Azov turbot, flounder, kilka, and zander. The life cycle features of the most abundant fishes are presented in Table 7.7.

In summer, the occurrence of increased concentrations of anchovy adults in the Kerch Strait and near-strait zone is 30%, that of eggs is 50%, and their larvae is met here in 50–70% of cases (Fashchuk et al. 1995).

Table 7.7 Biological state and behavior of main commercial fishes of the Kerch Strait throughout the year

Object	Season			
	Spring	Summer	Autumn	Winter
Goby	Migration to the coast for spawning in late March–early April ($T_w = 10°C$). Biomass is 20–60 kg/ha	From July to August (until November) adults and fingerlings feed in the zone of Port Krym–Port Kavkaz, Kerch Bay, SW coast of the strait	Feeding in the coastal zone of the strait until November. Then, migration to the deeper areas of the Sea of Azov	Wintering in the Sea of Azov, mainly outside the strait zone
Azov anchovy	In April ($T_w = 9–11°C$) within 20 days adults migrate through the strait as sparse shoals from wintering grounds in the Black Sea into the Sea of Azov for feeding and spawning. In May–June they are followed by juveniles	Until late July, spawning and feeding in the Sea of Azov outside the strait zone at $T_w = 18–26°C$ In July–September juveniles began to migrate back into the Black Sea	In September–November juveniles migrating into the Black Sea are joined by adults. Some shoals stay in the strait for more than a month. Under sharp cooling migrations are more active	Wintering in the eastern Black Sea outside the strait zone
Stripped mullet	In the middle of March fish enter the strait from the Black Sea, and in late April-early May mass migrations of shoals through the strait into the Sea of Azov for feeding is observed. In May–June adults leave the strait for spawning in the Black Sea	In July–September juveniles feed in the strait and Sea of Azov. Spawning of adults in the Black Sea outside the strait zone	In September juveniles and fingerlings migrate from the strait and Sea of Azov into the Black Sea for wintering.	Wintering in bays of the North Caucasus outside the strait zone
Golden mullet	In mid-March-early May fish migrate into the strait from the Black Sea side for feeding. In May–June adults leave the strait (until September) for spawning in the Black Sea	Feeding in the strait and Sea of Azov. In August–September adults leave the strait. From the second half of August (until November) fingerlings stay in the strait	In October–November immature individuals migrate from the strait into the Black Sea ($T_w = 12.4–16°C$)	Wintering in the Black Sea in bays of the Crimea outside the strait zone

(continued)

Table 7.7 (continued)

Object	Season			
	Spring	Summer	Autumn	Winter
Azov shad, Black Sea (Kerch) shad	From the middle, maximally from the end, of March-early April fish migrate into the strait from the Black Sea at $T_w = 4–5°C$ and higher. Large individuals enter the strait from early March to early May, and small individuals, from late March to late May	Feeding in the Sea of Azov until July. In late July the back migration of small forms through the strait into the Black Sea begins	Migration of large individuals into the Black Sea through the strait	Wintering in the Black Sea outside the strait zone

Photo 7.10 Black Sea turbot *Psetta maeotica* stay for awhile in the Kerch Strait for feeding only during the autumn season (photo by author)

In autumn, with seasonal cooling of the Sea of Azov, anchovy migrate via the Kerch Strait into the eastern Black Sea. Depending on the hydrometeorological conditions of the year, this process can begin in October–November, and the duration of migration via the strait ranges from 1 week to 1 month. The transition of surface temperature of the Sea of Azov through 10°C serves as a signal for the beginning of migration.

For striped mullet, two oppositely directed migrations via the Kerch Strait are observed in the spawning (summer) season. The first, pre-spawning, migration is from the Sea of Azov into the Black Sea for spawning, and the second, post-spawning, migration is from the Black Sea into the Sea of Azov for subsequent feeding.

In winter, most of fishes, except for small number of gobies, silverside, and kilka, leave the Kerch Strait and migrate to *the deeper areas of the Azov and Black Seas, and flounder begin to spawn in January-March*. Moreover, in August-October Black Sea scad and turbot (Photo 7.10) enter the strait for feeding, and kilka migrate from the Sea of Azov into the Black Sea for wintering.

After intensification of dumping of dredging grounds in the strait (increase in water turbidity) approaches of shad into the zones of its traditional fishery (the Tuzla Spit Island coast) during the periods of autumn (into the Black Sea) and spring (from the Black Sea into the Sea of Azov and further to the Don) migrations reduced. As a result, by 1968–1969 the catch of this species reduced 9 times; by

1971, 18 times; and by 1984–1986, 20 times, as compared with 1960. In 1990, the traditional shad fishing by drag-nets in the Kerch Strait was ceased because of the loss of commercial value by the population. Today, non-commercial catches of this species are fixed only occasionally in nets of coastal fishermen.

Thus, the Kerch Strait has the maximum fishery importance in spring (April–May) and autumn (August-November).

7.4 Natural Mechanisms of Environmental Condition Formation

Today the length of the Kerch Strait is 43 km along a straight line and 48 km along a navigational channel. The maximum width is 42 km, the minimum, in the northern part of the strait (in the area of Port Krym–Port Kavkaz), 3.7 km. The maximum depth at the strait entry from the Sea of Azov is 10.5 m; at the exit, 18 m. In the most part of its aquatory, except for navigational channel, depths do not exceed 5.5 m. The total area of the strait is 805 km^2, and water volume, 4.56 km^3. This exceeds the similar parameters of the Bosporus almost 20 and 3 times (Fig. 7.8).

Grounds in the central part of the strait are mainly sandy and sand-muddy; in the coastal zone of its southern part (Chushka Spit) they are muddy with shells and sand (Project “The Seas of the USSR” The Black Sea 1991a).

The analysis of biological information allowed us to establish that the state of the Kerch Strait and life activity of its inhabitants are determined by the sum of hydrometeorological factors, from which the wind regime, waves, water exchange and character of water circulation in the strait, thermal and ice conditions are priority.

7.4.1 Atmospheric Circulation and Water Dynamics

The long-term observations on wind regime at the coast of the Kerch Strait (HMS of Opasnoye, AMS of Kerch, settlement Zavetnoye) and adjacent areas of the Black Sea (HMS of Anapa) allowed establishing two oppositely directed prevailing wind flows over its aquatory: the northeasterly, easterly and southerly flows, and southwesterly flow. Each of them is formed under the certain type of atmospheric circulation over the whole aquatory of the Black Sea.

The north, northeast, and southwest types of atmospheric transfer have the highest annual frequency, equal to 11–13%. Its maxima for the sum of N and NE types (25–28%) and SW type (15–20%) are noted in winter months. The frequency of other types corresponding to remaining wind directions is distributed within a year uniformly and does not exceed 8% of cases per month (Chernyakova 1965).

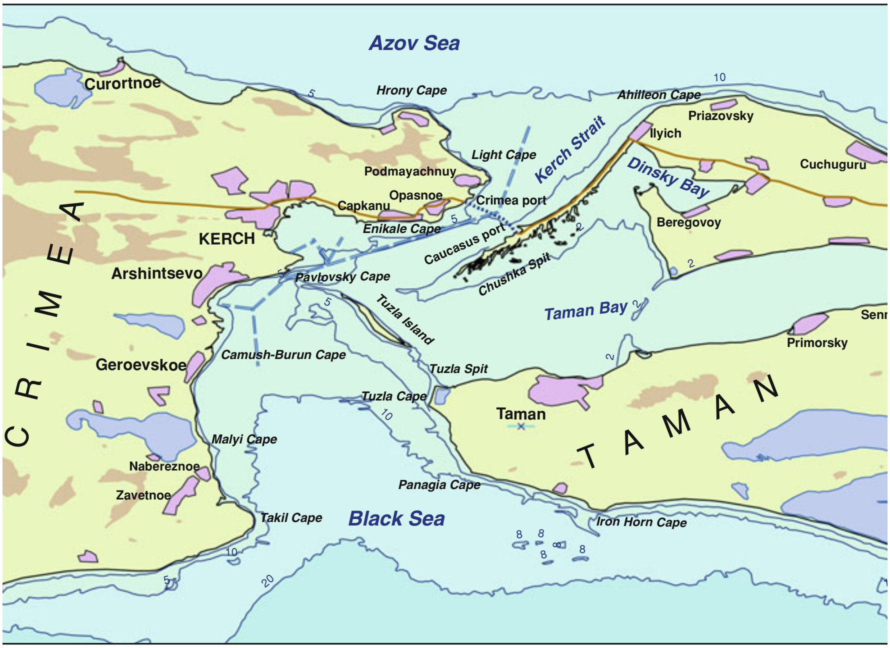


Fig. 7.8 The modern state of the Kerch Strait shoreline and bathymetry

Table 7.8 Mean monthly frequency (days) of winds in the Kerch Strait zone during 1952–1985 (Project "The Seas of the USSR" The Black Sea 1991a)

Direction	Months												
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Yearly mean
Northerly	18	16	18	14	14	14	16	18	18	18	17	17	16
Southerly	12	12	12	15	17	16	14	12	11	12	12	14	13
Calmness	1	0	1	1	1	1	1	1	1	1	1	1	1

At the development of N and NE type of atmospheric circulation over the Black Sea, winds of north quarter prevail immediately over the Kerch Strait aquatory, and under the SW type winds of south directions prevail over the strait (Table 7.8).

The mean annual number of cases with strong offshore winds in the northern and northeastern sea reaches 44–57 days, and in some years, 62–71 days. During the summer period such situations are observed up to 4 times per month, and in winter, up to 7 times per month. Within a year stormy winds in the Kerch-Tuapse and northwestern areas of the sea are registered in 34–35 cases, and in the area of the South Coast of Crimea, in 20–22 cases (up to 2 and 5 cases per month in summer and winter, respectively).

The character of wind activity over the Kerch Strait aquatory and physico-geographic features of the Sea of Azov determine the fact that its water exchange with the Black Sea occurs by means of reciprocating motions through the whole section of the strait, developing due to the level difference in its northern (Azov) and southern (Black Sea) parts. This difference can reach 100 cm and is formed as a result of runoff of the rivers running into the Sea of Azov, and offshore-inshore fluctuations caused by wind activity over the strait and Sea of Azov aquatories. The influence of wind on water level in the strait is on the average 5–6 times, and under the storms, 10–15 times more effective than the impact of river runoff. Thus, wind determines the short-term, while the river runoff, long-term variations in the intensity and character of water exchange between the Black and Azov Seas.

Under the winds of north quarter the strait level surface is inclined towards the Black Sea. In this case, the Azov type of currents is formed here (Fig. 7.9a). With progression from entry into the strait from the Sea of Azov side to the northern narrow, a gradual increase in the Azov current velocity

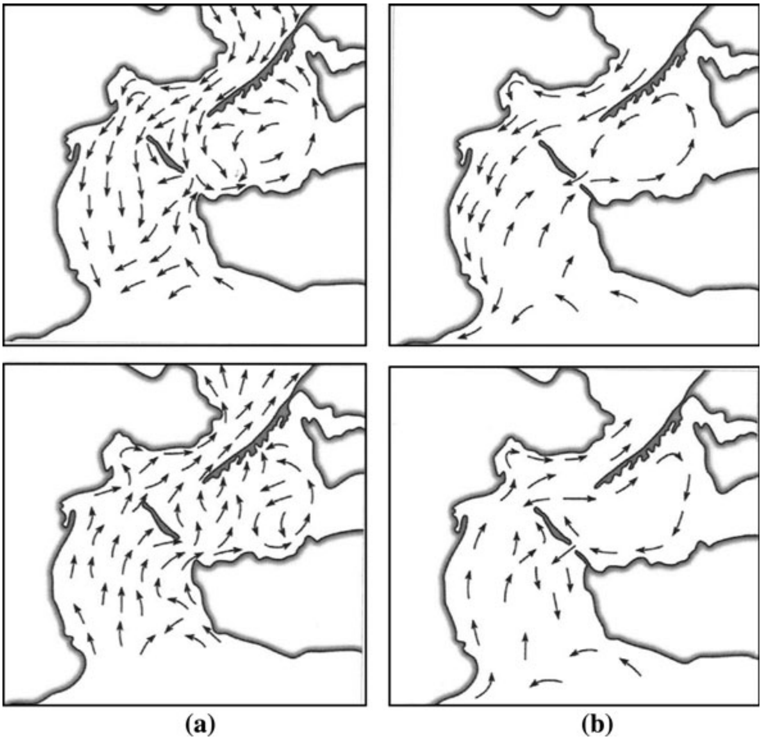


Fig. 7.9 Currents in the Kerch Strait under **a** the *north* (Azov flow) and **b***south* (Black Sea flow) atmospheric transfers before (*left*) and after (*right*) construction of the Tuzla Dam (Altman, 1987; Borovskaya, 2007)

(from 10 to 40 cm/s) is observed. Under the high and short-time surges from the Sea of Azov the northern narrow has not time to pass through all water surpluses piling up in this area, while their supply from the Sea of Azov still continues. The existent rise and cross slope of the sea level determine the development of countercurrent flow (in the near-bottom layer off the Russian coast) and flow of a portion of waters towards the Sea of Azov. This is accompanied by an increase in current velocity here up to 70–80 cm/s on the average. Further, the larger portion of the flow moves towards the Pavlovskaya Narrow, and the other portion, towards the Kerch Bay and Tuzla channel. The latter gives rise to cyclonic water circulation in the Taman Bay.

Under the winds of south quarter the strait level surface is inclined from the Black Sea towards the Sea of Azov. The Black Sea type of currents is formed (Fig. 7.9b). With the progression of the Black Sea flow to the central part of the strait its velocity increases from 10 to 40 cm/s, or 1.5 km/h. When approaching the Tuzla Spit Island, the current branches into two flows, one of which, a stronger one, is directed to the Pavlovskaya Narrow, while the weaker second flow, to the Tuzla channel. In the narrow zone and in the channel the current velocities increase up to 3 km/h. In case, if water volume is so large that an increase in velocity cannot provide the complete passage of waters to the central part of the strait, the countercurrent flow directed along the spit and eastern coast is formed as a result of backwater effect.

The mean annual occurrence of the Azov currents (to the Black Sea) is 58% of cases, and that of the Black Sea currents (to the Sea of Azov), 42% of cases (Table 7.9). Duration of the Azov currents induced by north wind can reach 300 h, and that of the Black Sea currents generated by winds of south quarter does not exceed 200 h.

The combined currents are observed on the average within 6–10 h. In the mean long-term context, the Azov currents are observed during 208 days, Black Sea currents, during 135 days, and combined currents, during 22 days. At the monthly scale, these values are 18, 11, and 2 days, respectively. In the areas of the

Table 7.9 Characteristics of water dynamics in the Kerch Strait under the different wind conditions (Project "The Seas of the USSR" The Black Sea 1991a)

Characteristic	Character of current		
	Azov (wind of north quarter)	Black Sea (wind of south quarter)	Combined (variable wind)
Annual occurrence	About 58%	About 42%	Less than 1%
Duration (max)	300 h	200 h	6–10 h
Duration (mean long-term)	208 days	135 days	22 days
Duration (mean monthly)	18 days	11 days	2 days
Maximum velocity (in the strait narrows)	0.7–0.8 m/s	0.7–0.8 m/s	0.4–0.5 m/s
Maximum velocity (in the wide strait areas)	0.4–0.5 m/s	0.4–0.5 m/s	0.1–0.3 m/s
Particle path per hour at maximum velocity (narrow/wide area of the strait)	2.5–2.9/ 1.5–1.8 km	2.5–2.9/ 1.5–1.8 km	1.5–1.8/ 0.4–1.2 km

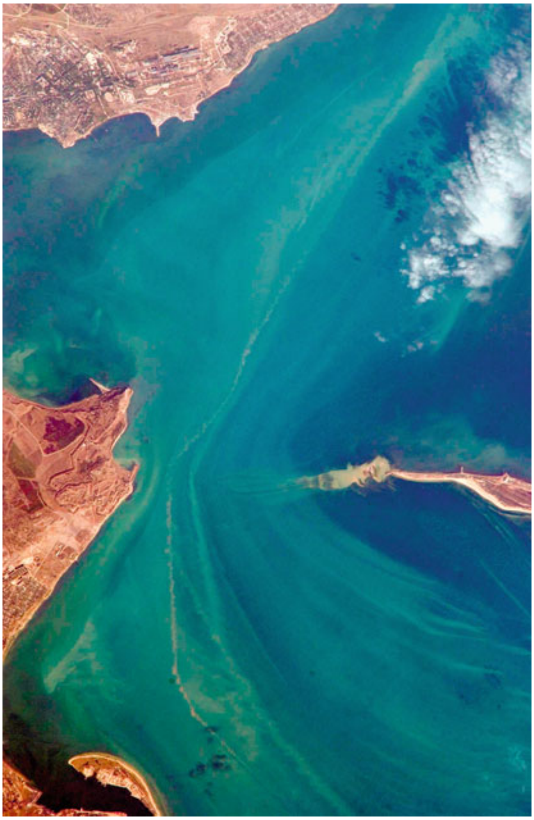


Photo 7.11 The Pavlovskaya Narrow of the Kerch Strait. *Left*—Cape Ak-Burun (*Cape White*); *right*—westernmost tip of the Tuzla Spit Island (photo from ISS)

Pavlovskaya Narrow (Photo 7.11) and Tuzla channel there is an increase in current velocity (up to 40 cm/s), associated with morphometric features of the area.

When leaving the narrow and the channel, waters rush to the Black Sea as a wide flow deviating to the Crimean coast. Towards the southern mouth of the strait, the current velocity decreases to 10 cm/s.

Having passed through the Pavlovskaya Narrow and the Tuzla channel, Black Sea waters fill the central part of the strait. The main jet of currents is headed northward but its portion enters the Kerch Bay. Near the northern narrow the confluence of all jets occurs, with the formation of intense flow of slightly transformed Black Sea waters. The banked up water level built in the Cape Enikale area causes an increase in slopes at the narrow tips. As a result, the current velocities here can exceed 3 km/h. When leaving the northern narrow, the current lessens and enters the Sea of Azov.

Because of complexity of the Kerch Strait coast orography, presence of islands here, and variability of wind field, eddy formations reaching 4–6 km in diameter in the northern narrow area and 1–2 km in diameter in the southern part of the strait, can be formed on its aquatory. The velocity of wind currents in the strait narrows can reach 0.7–0.8 m/s, with mean values of 0.25–0.35 m/s, while on the relatively wide sites it usually does not exceed 0.4–0.5 m/s, with mean velocity of 0.1–0.3 m/s (Altman 1987; Panov and Rubinshtein 1989).

7.4.2 Wind Waves and Water Exchange via the Strait

According to the long-term observations (1954–2002) at the Ukrainian HMS of Opasnoye, it follows that over the last 50 years the maximum wave heights (2–3 m) in the northern part of the strait were observed only 9 times (6 times in April, 2 times in June, and 1 time in July) under the winds of north quarter (Table 7.10).

Within a year (except for March) waves of 0.7–1 m height and lower prevail in the strait (44–51% of cases). The occurrence of waves with height of 1–2 m throughout the year ranges from 1 to 7.3%, with maxima from October to February (Yeremeev et al. 2003).

According to the field data, in the late 1980s the mean annual inflow of Azov waters to the Black sea through the Kerch Strait was 49.8 km^3, with the maximum of 71.2 km^3 (142% from the mean) observed in 1979, and minimum of 35.2 km^3 (71%) registered in 1973. The water outflow from the Black Sea on the average amounted to 33.4 km^3, ranging from 20.6 (1932) to 46.3 km^3 (1949), or 63 and 138% from the long-term mean. The resultant water exchange was directed from the Sea of Azov and on the average amounted to 16.4 km^3/year, with the maximum of 48.8 (1932) and minimum of 2.0 km^3 (1973) that in the former case reached 299% from the long-term mean (Altman 1987).

For most part of the year (except for spring months) the volume transport of the Black Sea currents exceeds that of the Azov currents (Table 7.11). However, in March–May the opposite situation is observed. In this period the volume transport of the Azov currents (340–860 m^3/s) become higher than that of the Black Sea currents. Thus, it may be supposed that in spring a significant role in this process (together with wind) is played by the regime of river runoff into the Sea of Azov. Floods favor an increase in velocities of currents from the Sea of Azov. During the period of instrumental observations on the components of water balance (1912–1975) a steady reduction in outflow of Azov waters to the Black Sea constituted 28.6, 22.3, 10.6, and 5.5 km^3/year for the periods of 1912–1922, 1941–1945, 1966–1975, and 1971–1975, respectively, was noted (Remizova 1984).

The analysis of long-term dynamics of water exchange through the strait by months showed that in 1971–1975 the volume transport of the Black Sea flow increased by 6.9 in April, by 6.0 in May, by 0.7 in June, by 2.0 in July, and by 0.7 m^3/month in August, as compared with the 1912–1948 period. The similar comparison for seasons allowed us to establish that over the investigated period during all seasons, except summer, the outflow of Azov water through the strait exceeded the inflow from the Black Sea by 5–16 km^3. With that, in autumn, 1971–1975 this difference (6.0 km^3) was almost the same as in 1912–1948

Table 7.10 Characteristics of maximum waves in the Kerch Strait for the 1954–2002 period by observations at HMS of Opasnoye (Yeremeev et al. 2003)

Characteristic	Months												Yearly mean
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
Height (m)	1.6	1.6	1.8	2.0	1.8	2.0	2.0	1.3	1.3	1.8	1.4	1.6	2.0
Direction	N, NE	NE	NE	NE	E, NE	NE	N	NE	NE	E, NE	N	NE	NE, E

Table 7.11 Intraannual dynamics of mean volume transport (m^3/s) in the Kerch Strait (Project "The Seas of the USSR" 1991a)

Flow	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Yearly mean
Azov (+)	3,640	4,650	3,420	3,990	3,820	3,720	3,620	3,120	2,320	3,060	3,360	3,370	3510
Black Sea (−)	4,170	6,700	2,560	3,650	3,480	4,190	3,480	3,550	3,320	3,820	4,010	4,300	3940
Σ	−530	−1,050	860	340	340	−470	140	−430	−1,000	−760	−650	−930	−430

Table 7.12 Dynamics of water balance components of the Sea of Azov (Ilyin et al. 2003)

Component of water balance (km^3)	Period			Trend (1923–1950) to (1951–1998)
	1923–1998	1923–1950	1951–1998	
River discharge	36.5	40.5	34.7	−5.8
Precipitation	15.2	15.0	15.3	0.3
Evaporation	33.0	33.3	32.9	−0.4
Outflow through the Kerch Strait	16.2	20.5	14.2	−6.3

Table 7.13 Mean monthly sea surface temperature in the northern part of the Kerch Strait by observations at HMS of Opasnoye (Project "The Seas of the USSR" 1991b)

Months												Yearly mean
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
1.9	1.0	2.5	8.0	15.3	21.1	24.1	24.1	20.1	14.3	9.0	4.6	12.2

(6.06 km^3), while in spring (3.48 and 17.32 km^3) the outflow from the Sea of Azov reduced five times due to regulation of the river discharge. In summer, 1912–1975 the Black Sea flow exceeded the Azov flow on the average by 7 km^3. In 1971–1975, this difference (9.97 km^3) increased by 2.5 km^3 in comparison with 1912–1948 (7.36 km^3) (Remizova 1984). By the data of recent observations at HMS of Opasnoye, the mean annual volume transport of the Black Sea current in the northern part of the Kerch Strait was 3,900 m^3/s, and that of the Azov current, 3,500 m^3/s. Nevertheless, owing to prevalence of the Azov current occurrence, the resultant annual flow is directed from the Sea of Azov, amounting to 12 km^3/year (Ilyin et al. 2003). By the results of balance calculations, this value is equal to 14 km^3/year. Compared to the period before regulation of the river discharge (1923–1950), during the next almost 50 years (1951–1998) it decreased by 6.3 km^3 (Table 7.12).

7.4.3 Thermohaline Conditions and Ice Regime

Sea surface temperature in the Kerch Strait varies from 0 to 2–4°C in winter and from 22 to 29°C in summer. The minimum strait-averaged water temperature on the surface is observed in January, while in the near-bottom, in March. Its maxima are reached in the whole water column in August. Homogenous vertical temperature profile is kept until December (Yeremeev et al. 2003). In the northern part of the strait (HMS of Opasnoye) the minimum sea surface temperature (1.0°C) is registered in February, and the maximum (24.1°C), in July–August (Table 7.13).

Winter advection of Azov waters with temperature close to freezing point into the Black Sea through the Kerch Strait leads to formation of the extensive zone of thermal front in the near-strait area, which determines distribution of the centers of life concentration of fodder zooplankton during this season.

Table 7.14 Mean dates and probability (*P*%) of characteristic ice processes in the Kerch Strait (HMS of Opasnoye) for the 1944–2003 period (Yeremeev et al. 2003)

Ice processes	Type of winter						Means for the whole period	
	Severe		Moderate		Mild			
	Date	*P* (%)	Date	*P* (%)	Date	*P* (%)	Date	*P* (%)
First ice formation	01.01	100	03.01	100	30.01	57	11.01	80
Steady ice formation	12.01	100	13.01	65	23.01	18	14.01	49
Beginning of formation of fast ice	15.01	82	09.01	40	17.01	11	12.01	34
First total freezing	13.01	91	20.01	80	27.01	14	18.01	51
Complete freezing	20.01	27	–	5	–	0	28.01	7
Beginning of fast ice fracturing	25.02	73	06.02	35	02.02	7	14.02	29
Complete destruction of fast ice	10.03	100	24.02	95	18.02	29	27.02	64
Complete ice clearing	29.03	100	07.03	100	23.02	57	08.03	80

Within a year mean sea surface salinity in the strait ranges from 14 (June) to 18.2‰ (January, November). The salinity minima in the near-bottom layer are noted in April and October. In January and November, the vertical salinity structure of the strait waters is homogenous.

As a result of water exchange with the Sea of Azov, mean annual salinity of coastal waters in the near-strait zone from the Black Sea side is minimum for the entire basin, 13.5‰ that is by 1‰ lower than in the coastal zone of the northwest shelf of the sea, subject to influence of the Danube runoff. At the same time, in the northern part of the strait, near the entry to the Sea of Azov, under the influence of its water exchange with the Black Sea salinity can change from 11.3 to 18.4‰ within several days.

According to the long-term observations at HMS of Opasnoye, the mean date of the beginning of ice formation in the Kerch Strait falls on January 11, with probability of 80%. However, it may vary from January 1 to January 30 for the severe and mild winter, respectively (Table 7.14).

In moderate and mild winters the complete freezing of the strait practically does not occur, and in severe winters it happens on January 20. The ice sheet is formed only in the northern part of the strait up to the Tuzla Spit Island, and thickness of fast ice in the Kerch Bay can reach 10 cm. In the Taman Bay ice is most persistent and can reach a thickness of 30 cm, and up to 65 cm in severe winters.

The complete clearance of ice in the strait occurs on the average by March 2008, with probability of 80%. In severe winters, this happens 3 weeks later (on March 29), while in mild winters, 2 weeks earlier (on February 23).

7.5 Economic Activity on the Strait Aquatory and its Consequences

Beginning from the post-war period and especially during the last years of the XX century, the Kerch strait has been affected by a rather intensive anthropogenic impact.

7.5.1 Transport Operations

At present, several large operating port complexes are located on the Ukrainian Coast of the Kerch Strait. They include: Kerch Commercial Sea Port, Kerch Fishery Sea Port, Port Krym, and port of Kamysh–Burun (Photo 7.12).

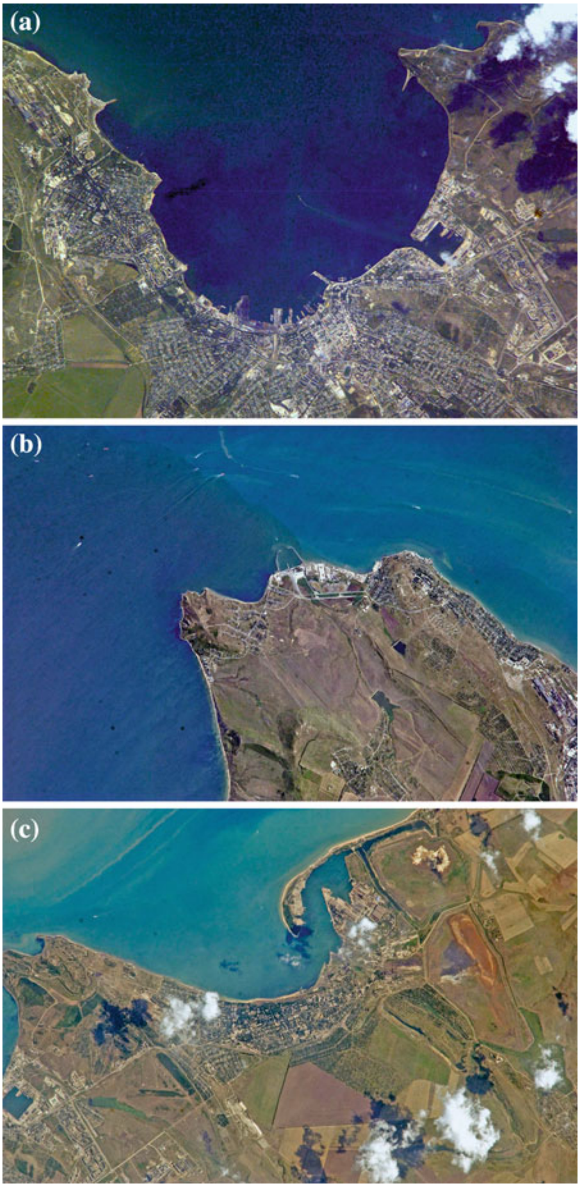


Photo 7.12 The Kerch Bay (**a**) with Commercial (*left*) and Fishery (*square at the right*) sea ports, Port Krym (**b**), and port of Kamysh—Burun (**c**) (photo from ISS)

Developing Port Kavkaz is located on the Chushka Spit from the Russian side of the strait. Moreover, the strait is crossed by maritime commercial routes connecting the ports of Ukraine and Russia situated on the coast of the Sea of Azov practically with all Mediterranean countries and many countries of the world. According to the data of Kerch maritime traffic regulation station, presented at the III International Research and Practice Conference "Environmental Problems and Features of Exploitation of Coastal Objects of Maritime Economic Complex" in 2003, from 1999 to 2002 the number of vessels passing through the Kerch-Enikalsky Channel excavated by Russia in the Kerch Strait in 1874, has increased from 10 to 20 thousand. According to the forecast, by 2005 this value should increase up to 30 thousand vessels (Blank et al. 2004).

From 1.5 billion t of oil equivalent containing in 120 oil-and-gas bearing structures of the Black Sea shelf of Ukraine, 21% is deposited in the Sea of Azov, about 17%, in the Kerch Strait area, and almost 40%, on the northwestern shelf between the Crimea and Snake Island (www.geonews.com.ua). The Black Sea mouth of the Kerch Strait (near-Kerch shelf) is one of the most promising oil-and gas bearing areas of the Black Sea. In 2004, State Joint Stock Company (SJSC) *Chernomorneftegaz* began and in January 2006 finished drilling of parametric well No. 403 in the Subbotino structure situated in this area. Oil was found at depth of 4,300 m under the seabed (depth of the sea is 40 m). The potential resources of this structure are estimated in 257 million t of oil equivalent. In 2007, the first exploratory well (3,200 m) was drilled and tested in the Subbotino oil field. The drilling confirmed its commercial oil reserves in amount of 100 million t. In 2008, SJSC *Chernomorneftegaz* drilled the second exploratory well here and began production testing of two wells. As yet two wells of the Subbotino oil site produce 406 millionm^3 of gas (about third of present production volume of *Chernomorneftegaz*). By 2016, it is planned to drill up to 80 wells here, from which 40 wells will be brought into production.

Taking into account the fact that today in the southwestern Sea of Azov (near the north mouth of the Kerch Strait) offshore hydrocarbon production is actively developed in the North Kerch, North Bulganak, and East Kazantip fields (up to 1 billion t of gas per year, with the volume of proven reserves of 10 billion t), and the fact that another 120 small offshore hydrocarbon fields were discovered in the same area (Krymskaya Gazeta 2004), it is logical to assume the future increase in intensity of oil product transportations through the strait by Ukraine.

Russian Port Kavkaz is situated on the Chushka Spit and occupies the strait aquatory with the area of 2.95 km^2 and depths of 5.4 m, artificially separated off by two wave-protecting piers. Port also possesses two anchorages: No. 454 at distance of 2 miles from the port and No. 451 at distance of 20 miles from the port in the southern part of the strait. The mineral fertilizer loading berth has length of 150 m and can provide services to vessels with draught of 3.9 m and freight-carrying capacity of 5,000 t. Anchorage No. 454 attends to vessels with freight-carrying capacity of 10–20 thousand t, and anchorage No. 451, up to 30–40 thousand t. Every day up to 50 tankers and other vessels are gathered on transshipment road near the strait mouth. Dynamics of the Russian maritime transportations of oil products through the Kerch Strait is also characterized by positive tendencies.

The Kerch Commercial Sea Port (KCSP) specializes in cargo handling and pilotage of vessels through the strait. The port has six berths with the total length of 1,904 m and fitted anchorage No. 471 in the southern part of the strait. The port provides services to vessels with maximum draught of 8.3 m and length up to 220 m. Six vessels with displacement of 40–50 thousand t and loaded draft up to 15 m can be maintained simultaneously at the anchorage. It is planned to expand this anchorage for maintenance up to 20 vessels simultaneously.

In 1980–1990, the Kerch Commercial Sea Port shipped the industrial equipment, construction materials, agricultural production, and other goods by sea to Turkey, Greece, Syria, Lebanon, Italy, and Cyprus. For example, from 1998 to 2004 the amount of loose goods transshipped in the Kerch Commercial Port increased almost four times, from 650 to 2,300 thousand t. Since 1990 half of cargo shipped from the Kerch Commercial Port is provided by industrial plants of Russia: Novolipetsk and Staryoskolski Steels Old Oskolsky deliver steel coils and pellets, factories of Nizhni Tagil and Saratov, steel feed. Through the Kerch Commercial Port Ukraine exports ferromanganese and ferrosilicon from Mariupol and glass from Lisichansk to the Mediterranean countries. In recent years India and Taiwan (metals), the USA (pellets, steel feed), Algeria and Egypt (glass) became maritime trading partners of Russia and Ukraine (Mochulsky 1996). Thus, the total volume of cargo transported by Ukraine and Russia through the channel within a year exceeds 550 million t. From this volume, oil products constitute more than 10 million t.

After disintegration of the USSR only 5 out of 25 seaports of the Azov–Black Sea basin belong to Russia. They are Taganrog, Temryuk, Novorossisk, Tuapse, and Sochi. To maintain handling and transportation of the specified volume of oil products and other general cargo of wide range through the Kerch Strait, it is planned to bring the total cargo turnover of the Temryuk port and developing ports of Kavkaz and Yeysk by 2020 to 12–15 million t (4–5 million t for each port). The cargo turnover of the new oil transshipment terminal under construction at the exit from the Kerch Strait to the Black Sea (settlement Zhelezny Rog, Krasnodar territory) will be 9.5 million t. The prospective cargo turnover of Russian Black Sea ports carrying out the similar operations will amount to (for comparison) 34 and 60 million t in Novorossisk, and 14 and 19 million t of dry and bulk cargoes, respectively (Litvinenko et al. 2001).

7.5.2 Transshipment and Pumping Transfer of Cargo

The depth of the Kerch-Enikalsky Channel (9 m) does not allow vessels with displacement of 50 thousand t and more (length of 140–200 m) to be loaded completely. The maximum loading of any transport sailing by the channel through the Kerch Strait does not exceed 25,000 t, and the cost of its pilotage is US $3500.

Thereupon, on the strait aquatory and in its south mouth, in the zones of Ukraine and Russia at anchorages Nos. 471, 451, and 454, low-tonnage vessels, as several centuries ago, transship coal, coke, soda ash, scrap metal, ferroalloys, and grain delivered from the Azov Sea ports on ocean superliners.

In 2002–2003, the total cargo transshipment by Ukraine on the outer road of the Kerch Strait reached 6 million t, from which oil products constituted 3.4 million t; gas block sulfur, 1.3 million t; grain, about 1 million t; and mineral fertilizers, more than 0.25 million t. Compared to 2002, the volume of transshipments of oil in 2003 increased 5 times; oil residue, 2.4 times; sulfur, 2 times; and mineral fertilizers, 1.4 times (Blank et al. 2004).

Oil products transported by Russia through the Kerch–Enikalsky Channel are delivered from the Caspian Sea by low-tonnage (5,000 t) bulk barges of the "river-sea" type, with draft of 3.4 m (up to 2,000 barges/year). The annual volume of such transportations reaches 10 million t. Since 1990, at anchorages No. 451 and No. 454, together with transshipment of dry cargo, the earlier prohibited pumping transfer of oil products began to be carried out.

Transport operations under oil exportation through the strait and its transshipment at the strait entry are accompanied by unavoidable losses of oil products both as a result of unauthorized disposals at washing of tanker holds and losses in the process of pumping transfer and due to casualties on trading and bulk-oil vessels waiting for pilotage or sailing by the channel. Russia transports the Caspian oil beyond the Kerch-Enikalsky Channel by parallel waterway. The depths here do not exceed 5 m, and sea bottom is sown with projectiles "passed through artillery tube", which remained after the war. To rise the efficiency of transportations, it is planned to increase a draft (loading) of tankers of the "river-sea" type up to 4.4 m. It is difficult to overestimate the scales of possible consequences of the 5,000 t oil spillage for inhabitants of the strait coast and hydrobionts living in its water in case of explosion or wreck of such tanker.

7.5.3 Dredging and Dumping of Grounds

The first dumping of ground in the Kerch Strait was organized in 1956. Until recently four dumping zones were located here. They almost did not affect the ecological situation as the volumes of dredging were small. However, in the late 1980s the volume of dumped grounds reached 1.0–5.0 million m^3, and the anthropogenic changes of marine environment in dumping sites began to exceed, by their scales, a natural background (Petrenko et al. 2002). For this reason at the end of the XX century in the coastal zone of the Sea of Azov and Kerch Strait the processes of mud accumulation and export of deposits to the strait intensified. The rate of sedimentation here is 30–40 times higher than rate of natural sedimentogenesis.

In 1961–1963, the accumulation rate of fine bottom sediment material in dumping zones was 0.15 cm/year. In 1964–1970 it increased eigh times (1.2 cm/year), and by the time of relocation of dumps it equaled 0.29–0.65 cm/year

(Rubinshtein and Khizhnyak 1988). As a result, since the mid-1970s the degradation of mussel population was observed here. From the early 1950s to the mid 1960s their stock reduced from 100 to 50 thousand t. In 1979 it was 15,000 t, and in 1989, only 2,000 t. The mussel stock in the near-strait zone in this time decreased from 300 to 78 thousand t. In the late 1980s the mussel harvesting in the Kerch Strait and near-strait zone was ceased (Fashchuk et al. 1991). At present, the biocenosis of mussels (*Mytilus galloprovincialis*) is located in the northern part of the area and near the navigational channel.

After intensification of dumping of dredging grounds into the strait (increase in water turbidity) the approaches of shad to the zones of traditional fishery (the Tuzla Spit Island coast) during the periods of their autumn (into Black sea) and spring (from the Black Sea into the Sea of Azov and further to the Don) migrations reduced. As a result, by 1968–1969 the catch of this species decreased 9 times; by 1971, 18 times; and by 1984–1986, 20 times, as compared with 1960. Thereupon, from 1987, upon the recommendation of YugNIRO dumping of grounds in the strait was ceased. The zone of their burial was relocated on depth of 50 m in the near-strait area of the Black Sea shelf.

Nevertheless, in 1990, the traditional shad fishing by drag-nets in the Kerch Strait was ceased because the population lost its commercial importance. At present, small catches of this species are occasionally fixed in nets of coastal fishermen.

7.5.4 Oil and Chemical Pollution of Water and Bottom Sediments

According to field observations carried out by YugNIRO in 2002, the oil product content in water column of the Kerch Strait varied from 0.02 to 0.12 mg/L (2.5 MACs) that coincided with results of oil pollution monitoring obtained by specialists of HMS of Opasnoye. The mean values of this characteristic at latest measurements amounted to 2 MACs, and the maximum concentrations reached 5.8 MACs and were fixed in the central part of the strait (Yeremeev et al. 2003). The concentrations of detergents, phenols, and toxic heavy metals, such as arsenic, chrome, cadmium, in the strait water on the average do not exceed the corresponding MAC levels, while, according to the data of YugNIRO, the mercury and lead content in the larger part of the strait in 2002 was above the allowable level.

According to the YugNIRO data obtained in 2002, the oil product content in bottom sediments of the strait was on the average 0.398 mg/g of dry weight. The concentrations of arsenic, lead, and cadmium here exceeded the GBV for the Azov-Black Sea basin. After relocation of ground dump from the Cape Tuzla area (southeastern, Russian part of the strait) into the deeper near-strait zone (isobath of 50 m) the OCP content in bottom sediments decreased from 0.45 μg/g of dry weight to almost zero value (Tretyakova et al. 1993).

By value of the index of water pollution (IWP), in 2002, Kerch Strait waters were classified as moderately polluted (IWP = 0.84). The content of inorganic forms of nitrogen, total nitrogen and phosphorus in the strait waters did not exceed the MAC value, though the concentration of ammonium nitrogen increased by factor of 1.5, compared to 2001 (Yeremeev et al. 2003).

7.5.5 Present Attempt to Dam the Tuzla Channel

Geopolitically, the possession of the Tuzla Spit Island situated between the Kerch and Taman Peninsulas allows Ukraine to control both vessel traffic in the Kerch Strait and resources (fishery, mineral) concentrated in the southern Sea of Azov. For example, until 2003 Ukraine received annually US $15–20 million for navigation of only Russian vessels in the Kerch–Enikalsky Channel (according to the Ukrainian sources, up to US $900 million) (Bekyashev and Bekyashev 2003). Moreover, more than 100 small and 7 relatively large offshore oil-and-gas fields were discovered in the southeastern Sea of Azov, near the north mouth of the Kerch Strait along its Azov coast. Three of them (gas fields) are already developed by Ukraine (Krymskaya Gazeta 2004).

On November 28, 1869 the Decree of Russian Senate incorporated de jure the Middle Spit (Tuzla) as a part of the Kuban Region. 53 years later, on July 13, 1922, by the Resolution of the All-Russian Central Executive Committee (VTsIK) Tuzla was included in structure of the Crimean Region. 20 years later, on January 7, 1941, the Decision of the Presidium of the Supreme Soviet of the RSFSR “On Transfer of the Middle Spit (Tuzla) from Temryuk District of the Krasnodar Territory in the Structure of the Crimean ASSR” was adopted. With that, the settlement of the Middle Spit Island was subordinated to the Kerch City Soviet of Working People’s Deputies.

In 1954, by another Decree of the Presidium of the Supreme Soviet of the USSR the continental part of the Crimean Region was transferred in administrative subordination of the Ukrainian SSR. In the early 1970s the territorial and regional authorities of the Krasnodar Territory and the Crimean Region coordinated the border between these administrative formations of the RSFSR and the Ukrainian SSR. With that, the maritime border was marked on the Kerch Strait aquatory, and a part of the Tuzla Spit Island was included in the Crimean Region. After disintegration of the USSR, Ukraine unilaterally declared this administrative borderline as the state border. Despite the Treaty of Friendship, Cooperation and Partnership between Ukraine and the Russian Federation signed on May 31, 1997, up to December 2003 the Russian Party did not recognize the existence of such border in the Kerch Strait (Bekyashev and Bekyashev 2003).

On January 28, 2003 Ukraine and the Russian Federation signed the Agreement on Ukranian–Russian state border which, nevertheless, did not resolved dispute on such border in the Kerch Strait. In October–November 2003 from the Russian coast of the strait the construction of dam for its closure east of the Tuzla Spit

Photo 7.13 Tuzla dam constructed from the Russian side of the Kerch Strait in October–November 2003 (Photo by author)

Island has begun (Photo 7.13). The arguments of dam construction were as follows: prevention of erosion of core part of the Tuzla Spit Island; prevention of emergency situations (inundation) which became more frequent in recent years on the 9 km site of the Taman Peninsula in Cossack village of Taman, settlements Primorsky and Sennoy; and liquidation of flood hazard to archaeological sites and residential buildings of the Temryuk and other coastal districts of the Krasnodar Territory. Ukraine, from its part of the Tuzla Spit Island, started to deepen with dredger the remaining passage between the island and Russian dam, dumping every day 2,500 m^3 of sea ground to the Russian coast (Bekyashev and Bekyashev 2003).

On December 27, 2003, during a visit of President of the Russian Federation in Kerch, two countries signed the Bilateral Agreement on Cooperation in Use of the Sea of Azov and the Kerch Strait. It states that these sea areas are historically internal waters of Ukraine and the Russian Federation.

With that, the Sea of Azov is delimited by state borderline under the contract of January 28, 2003 and “settlement of disputable problems concerning the Kerch Strait aquatory is administered under the Ukranian–Russian agreement” (Kerchensky Rabochii 2003). Hereupon, the construction of the Tuzla dam was suspended. However, so far the author does not have any information about ratification of the last document by the Governments of both countries.

7.6 Possible Hydroecological Consequences of Tuzla Channel Damming

The process of the Tuzla Spit erosion begun about 300 years ago in the eastern part of the strait ended with its breaking and transformation into an island after the strong Black Sea storm occurred on November 29, 1925. In 25 years (by 1950) the width of the Tuzla channel formed after the storm (300 m) increased up to 3 km, and in the late 1970s it was almost 4 km (Boldyrev 1958). Thus, the natural processes of silting deposit differentiation on each side of the spit supported conservation of its rests in the form of the Tuzla Island. Today its length, depending on the position of water level in the strait, varies from 6.5 to 7 km, the maximum width is 500 m.

7.6.1 Plans of Artificial Regulation of Water Exchange via the Kerch Strait in the Late XX Century

By the end of 1970s the total irretrievable withdrawal of river discharge into the Sea of Azov reached 9–12 km^3/year. As a result, the ratio of water inflow from the Black Sea through the Kerch Strait to its outflow from the Sea of Azov increased from 0.68 to 0.85 (Belov et al. 1978). Over 8 years salinity of the latter increased from 10.5 to 12.4‰, its nutrient balance was disrupted, oxygen regime deteriorated, and the level of biological productivity in the sea sharply decreased.

The complex of hydroeconomic measures on optimization of hydrological regime of the Sea of Azov, along with river flow transfer from other basins, included the plan of construction (by 1990) of regulator in Kerch strait, a dam for artificial restriction of saline Black Sea water inflow into the sea, decrease and further maintenance of its salinity at an optimum level.

The possible hydrological consequences of an attempt to dam the Tuzla channel were predicted in 1977 by specialists of the State Oceanographic Institute. By the mix formula and the equation of salt-water balance, future (2000) salinity of the Taman Bay and the Sea of Azov in a case of landfilling of the Tuzla channel in 1980, was calculated (Altman and Agarkov 1981). When calculating, water salinity in the near-strait area of the Black Sea was taken as constant and equal to 17.9‰; initial mean long-term salinity of the Taman Bay, 15.6‰; salinity of the Sea of Azov in 1980, 15.93‰; and the mean volume transport of the Black Sea and Azov currents in 1980, 34.3 and 46.0 km^3. The calculations showed that with account of climatic variations and tendencies in anthropogenic withdrawal of river discharge into the Sea of Azov in 1980–2000, 20 years after the damming of the Tuzla channel salinity of the Taman Bay would decrease by 0.45‰, from 16.56 to 16.10‰, while without damming it would decrease by 0.76‰, from 17.01 to 16.77. Thus, damming of the channel reduces a rate of the Taman Bay freshening under the influence of natural and anthropogenic components of water balance of the sea of Azov by a factor of 2.

At the same time, the calculations showed that after the construction of dam in the Tuzla channel the annual inflow of salts into the Sea of Azov would decrease by 1% only (below accuracy of model calculations) that evidenced a safety of this action for salt balance of the sea (Altman and Agarkov 1981).

The forecast of possible consequences of dam construction for the Sea of Azov was developed on the basis of calculations by mathematical model of water and salt balance of the sea, taking into account the volumes of river discharge, its intraannual distribution and total prospective withdrawals, as well as the similar distribution of precipitation, evaporation, wind conditions, and level fluctuations (Shlygin 1979).

After realization of 25 model scenarios considering the regime of discharge withdrawal (30 years in each time series), the prognostic (up to 2006) numerical variants of disposal of Azov water or release of Black Sea water (at the mean river discharge of 28 km^3/year) ensuring a decrease in ratio of their volumes from 0.7 to 0.2 and maintenance of mean sea salinity at the level of 9.5–10.5‰, were obtained. The diagram of relationship of integral time of opening of overflow sluice of hydrosystem for fish passage in spring (into the Sea of Azov) and in autumn (into the Black sea) with the volume of river discharge and salinity of the Sea of Azov was constructed. In either case it varied from 400 to 900 h, depending on values of the specified parameters. The specified model developments were not realized in practice because the design of Kerch dam construction was not approved by the Russian Government.

7.6.2 Changes in Environmental Conditions and Behavior of Commercial Hydrobionts After Natural Breaking of the Tuzla Spit in 1925

In the first days of the Tuzla channel formation after the storm on November 25, 1925 its width did not exceed 300 m. By September 1926, the channel between the formed Tuzla Island and the rests of the spit on the Taman Peninsula widened up to 940 m. Harbor engineers feared that this could affect the hydrological regime and character of water circulation in the Kerch Strait determining the dynamics of silting deposits in its central part and in the Kerch Bay. Thus, in the 1920s the question on fixation of the Tuzla Spit Island and landfilling of the formed channel was raised (Altman and Agarkov 1981).

The analysis of spit breaking effects on the hydrological regime of the Kerch Strait allowed us to establish that its essential changes occurred only in the southern part and Taman Bay. The regime of the northern areas remained almost unchanged (Berenbeim 1955, Nadezhin 1947). *Before the formation of channel* the southern part of the strait, even in periods of the Azov current development, was under the persistent influence of relatively warm and saline Black Sea waters. Entering the strait along its eastern Caucasian coast, they formed stable cyclonic circulations, warm and saline “life oases”, off the Tuzla Spit during all seasons of the year. Herewith, the Taman Bay represented “backwater” because it water exchange with transit Black Sea waters occurred through the along-strait section from the Chushka Spit to the Tuzla Spit was very insignificant.

Thus, until 1925 the Tuzla Spit was a natural barrier in the southern part of the Kerch Strait which favored the autumn concentration of fish shoals migrating from the Azov to the Black Sea for wintering, at the mouth of the Taman Bay along the Kuban coast (at Belyi scarp and Gadyuchyi Kut bog). From here fish moved westward along the Tuzla Spit to the Pavlovskaya Narrow and then into the Black Sea. In spring the Tuzla Spit also directed mullet, some number of shad, goatfish, and anchovy juveniles migrating at this time from the Black Sea to the Sea of Azov for feeding, to the Pavlovaskaya Narrow. Herewith, fish shoals concentrated in the area of the Kamysh–Burun Spit (Karbasnikov 1929; Treshchev 1945).

After the spit breaking cold freshened waters from the Sea of Azov and the Taman Bay began to reach the Caucasian coast of the southern strait through the formed channel in autumn, winter, and early spring, and the bay itself transformed from the stagnant to relatively running-water water body. After this event 10–20% of transit water volumes of the entire strait, reaching 6,000–7,000 m^3/s, began to pass through the Tuzla channel that was close to the volume transport across the section from the Chushka Spit to the Tuzla Spit.

As a result of the spit breaking, the routes of autumn and spring migrations of fish changes essentially. Species wintering off the Caucasian coast of the Black Sea began to move there and return in spring into the Sea of Azov for feeding mainly by the shortest route through the Tuzla channel that reduced probability, duration and changed the terms of their concentration in the Taman Bay and along the western coast of the strait at the Kamysh–Burun Spit (Berenbeim 1955).

7.6.3 Possible and Actual Changes in Environmental Conditions After Construction of the Tuzla Dam in 2003

Now the construction of the dam started in October–November 2003 is stopped but the channel width between the Tuzla Island and the Kuban coast has reduced from almost 4 km to 300 m (Photo 7.14).

Until October 2003 the regular dredging works on waterway maintenance, activity of transshipment roads (including transshipment of chemical raw materials) and ports have affected the Kerch Strait aquatory, excepting the “channel” east of the Tuzla Spit Island. In the process of dam construction and deepening of

Photo 7.14 After construction of dam in 2003, width of the Tuzla channel does not exceed 300 m (photo from ISS)

the channel between it and the Tuzla Island a volley of suspensions into the strait occurred here for the first time. Their sedimentation over the large areas undoubtedly resulted in deterioration of habitat conditions of bottom organisms and vegetation (Fashchuk and Petrenko 2008).

Moreover, after the dam construction in 2003 the essential changes occurred in the water circulation system of the Kerch strait. They were reflected first of all in the character of deposition in the strait and intensity of abrasive coastal processes. The remote (satellite) observations on the Kerch Strait currents by methodology developed by Ukrainian scientists from Marine Hydrophysical Institute (Sevastopol), and visual observations on the dynamics of a coastline at the Kerch strait coast in 2003–2007 allowed fixing the considerable changes both in the character of water circulation and state of beaches on the strait coast (Borovskaya 2007). Under north and northeast winds, velocity of the Azov currents along the Crimean coast of the strait increases substantially (see Fig. 7.9a, right) because a barrier in form of dam does not allow the southern stream to be distributed uniformly over the strait aquatory. As a result, for 3 years (2004–2006) on the considerable part of the strait coast south of Kerch to Cape Takil sandy beaches were washed away inland by 10–20 m. This caused submergence of coastal boarding houses and caving of shoreface in some places (Photo 7.15).

After deciphering of satellite images, it became obvious that construction of the Tuzla dam has changed the structure of water circulation in the strait. Under the south winds Black Sea waters began to inflow in the Taman Bay not through the Tuzla channel but across the along-strait section from the Tuzla Spit Island to the Chushka Spit only after passing of the Pavlovskaya Narrow. As a result, in these periods, the cyclonic type of circulation in the bay (counterclockwise) was replaced by opposite, anticyclonic, circulation favoring accumulation of suspended matter in the strait and, consequently, its silting. Moreover, the uncompleted dam became a barrier for Black Sea waters and promoted, under the south winds, development of the southern countercurrent flow along the Taman coast (see Fig. 7.9b, right) and local anticyclonic circulation in the southern strait from

Photo 7.15 Sea cliff with the rests of beach and signs of caving (talus) on the Crimean coast in the southern Kerch near settlement Zavetnoye (photo by author)

the Black Sea side of the dam that undoubtedly should affect both the sedimentation regime and ecological conditions in this area.

7.6.4 Possible Changes in Fish Behavior After Construction of the Tuzla Dam in 2003

The performed analysis of biological and life cycle features of inhabitants of the Kerch Strait waters allowed us to assess the possible ecological consequences of connection of the Tuzla Spit Island with the Taman Peninsula, which improved the conclusions made in the 1920s–1950s.

The dam construction will affect negatively first of all those species which during their migrations feed on the shallow sites of the strait, rich in detritus and fodder benthos, and spawn in their mass on its aquatory and in adjacent areas of the Sea of Azov. These objects include *haarder, local Black Sea mullets (striped, golden, and gray mullets), and goatfish.* Because of its adherence to lay eggs on coastal aquatic vegetation, *garfish* also can be referred to this group of “affected” species. The more so, as its spawning grounds in the Sea of Azov is limited by a very small zone with increased salinity, directly adjacent to the strait.

The intensification of sedimentation process in the Taman Bay and on the strait aquatory north of the dam and Tuzla Spit Coast will cause a need of more frequent cleaning of navigable waterways. Dumping in the strait and adjacent areas of the sea will increase. Silting of habitations of bottom hydrobionts, destruction of underwater landscapes will produce the maximum harm to *haarder* and *local mullets* migrating through the strait.

Because of the loss of water self-cleaning capacity there will be no more a continuous “live corridor” in the strait for migrating fishes. Thereupon, *goatfishes* which constantly reside in the near-bottom layer and feed on benthic organisms can reduce frequency of their migrations through the strait into the Sea of Azov for feeding. Moreover, shallow feeding grounds of *haarder* and local mullets in the Taman Bay will become less available. The food base of *gobies* entering the strait from the Sea of Azov will decrease.

One of serious adverse consequences of the complete “channel” damming may be associated with reduction in scales or even termination of haarder spawning migrations into the southern, more saline area of the strait and adjacent part of the Black Sea. As the northern strait will become even closer by its salinity to the Sea of Azov, fish, having entered the strait and without having found usual migratory route, cannot spawn here, and their reproductive products resorb. Or eggs laid in low-density water will gravitate to the bottom, where their development ceases. Certainly, the Azov population of haarder has also other spawning areas located in limans of the North Azov. However, deterioration of reproduction conditions in the only area of the southern half of the sea, suitable for spawning by its salinity, reduces in whole the probability of successful reproduction of this species.

The lessening of water exchange in the strait at the dam reaching of the Tuzla Island will result in general deterioration of the ecological situation in the northern strait and possibly even in the southern Sea of Azov. The forecasted development of near-bottom hypoxia zone north of the dam, against an increased entry of silts and bottom organic deposits, will create preconditions to formation of extensive suffocation zone here in summer. In parallel, the accumulation of toxic substances will occur in this strait area. In addition, these substances will come strenuously in water due to secondary pollution under the dredging operations. In this situation all near-bottom and coastal fish species (*gobies, flounder, mullets, goatfish, haarder*, etc.) will be certainly affected.

The negative impact of dam constructed in the Tuzla Island area will be felt by specially protected (written in the Red Book) species of hydrobionts because they either are very exacting to sea water quality (*salmon*) or belong to groups of near-bottom and coastal species (*mousefish*, *seahorse*, *beluga*, *gurnard*, etc.), very sensitive to the character of sedimentation and water turbidity.

Anchovy as a heat-loving species will primarily feel the changes in temperature regime of the strait (Budnichenko and Chashchina 2000). The increased ice cover of the northern strait during the autumn–winter period will lead in some years to delay in spring anchovy migration, and at the complete connection of the dam with the island the cases of their concentration in the Taman Bay where they can perish from sharp autumn cooling, will be observed more often. Nevertheless, as such situations have been noted not infrequently before 1925 and are usual for this species, it is difficult to assume that decline of population under the temperature factor exceeds the mean level of natural mortality.

The consequences for commercial stock of *Kerch (Don) shad* will be also insignificant. This object is also not related to the strait in terms of feeding or reproduction. At sharp water temperature falls in autumn, shad always rather intensively migrate through the Kerch Strait. The scales of their spring migrations into the Sea of Azov and further into the Don depend entirely on abundance of fish reached the age of sexual maturity and accumulated enough energy during the feeding period in the Black Sea. With that, the part of population feeding on anchovy during wintering returns to the Sea of Azov together with this species. Correspondingly, migrating shad, as anchovy, keep the strait sites which are close to waterway. Thus, the role of Tuzla channel for shad migration is small. Moreover, this fish is more cold-tolerant than anchovy.

It is unlikely to expect serious negative consequences of dam construction for *silverside*. It migrates uniformly in all strait areas and is characterized by a large degree of euryphagia, it easily changes from one type of food to another, utilizing the whole water column. The dam will not affect essentially on the stock of other abundant fish, *scad* which enters the Sea of Azov sporadically and in numbers constituting only a small part of the whole population. Being a high-speed pelagic species, they easily pass the strait and are distributed mainly in the southern Sea of Azov, leaving it with the first water cooling in September.

7.7 Conclusion

The geographic and ecological model of the Kerch Strait may serve as a basis for making of nature conservation decisions or identification of directions for research of possible consequences in case of various changes in environmental conditions in the strait (see Chap. 8). Nevertheless, taking into account the high current rates of changes in marine environmental conditions under the influence of both natural and anthropogenic factors, it, certainly, needs a constant updating, i.e., supplementation by new information. Herewith, it seems appropriate to organize the regular monitoring of environmental conditions along the whole Russian coast of the strait. Today such control is carried out by divisions of the hydrometeorological service of Ukraine (HMS of *Opasnoye*, MHS of *Kerch*, MHS of *Zavetnoye*). For known reasons these data are not readily available. Only one Russian observation station (MHS of *Taman*) situated on the eastern coast of the Kerch Strait and conducts the local marine observations on level, water temperature and salinity, waves, and ice conditions from the coast, which are insufficient for adequate reflection of ecosystem state in this important natural and economic sea region.

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Chapter 8
Wreck of the Tanker *Volgoneft-139* in the Kerch Strait on November 11, 2007

In Chap. 2 of the monograph, the calculated trajectories of oil product slick in the Kerch Strait under the influence of different wind situations and prevailing currents in case of the hypothetical 1500 t oil spill in consequence of the tanker wreck were shown as an illustration of the prognostic marine ecological maps. By a twist of fate, on November 11, 2007 during the extreme storm in the strait the tanker *Volgoneft-139* which stood at the anchorage broke in two, and more than 1000 t of fuel oil came into the sea *de facto*. We made the analysis of this accident on the basis of geographic ecological research and prognostic calculations by hydrodynamic model of oil spill *SPILLMOD* (Fashchuk 2008, 2009; Ovsienko et al. 2008).

8.1 Hydrometeorological Conditions of the Wreck

On November 8–10, 2007, after a sharp deepening of the cyclone centered over the Baltic Sea, the inflow of warm air from the south intensified in its frontal part, while the outbreaks of cold air into the southern areas of Europe, including aquatories of the Black and Azov Seas appeared on the SE periphery of this cyclone, became more active in a rear of the low (Fig. 8.1a).

As a result of such transformations of the baric field and strengthening of atmospheric flows, on November 10, 2007 a deep cyclone began to develop over Italy, which with its further deepening displaced towards the Balkans, being accompanied by storm rainfall, thunderstorms and E-SE winds with speed of 7–11 m/s (in the western Black Sea, 12–17 m/s, and on the evening of November 10, up to 22 m/s). With that, air temperature along the cyclone line rose from 3 to 8°C.

On the night of November 10–11 the cyclone reached the Black Sea aquatory and swept towards the Crimea with speed of 70 km/h (Fig. 8.1b). With that, the

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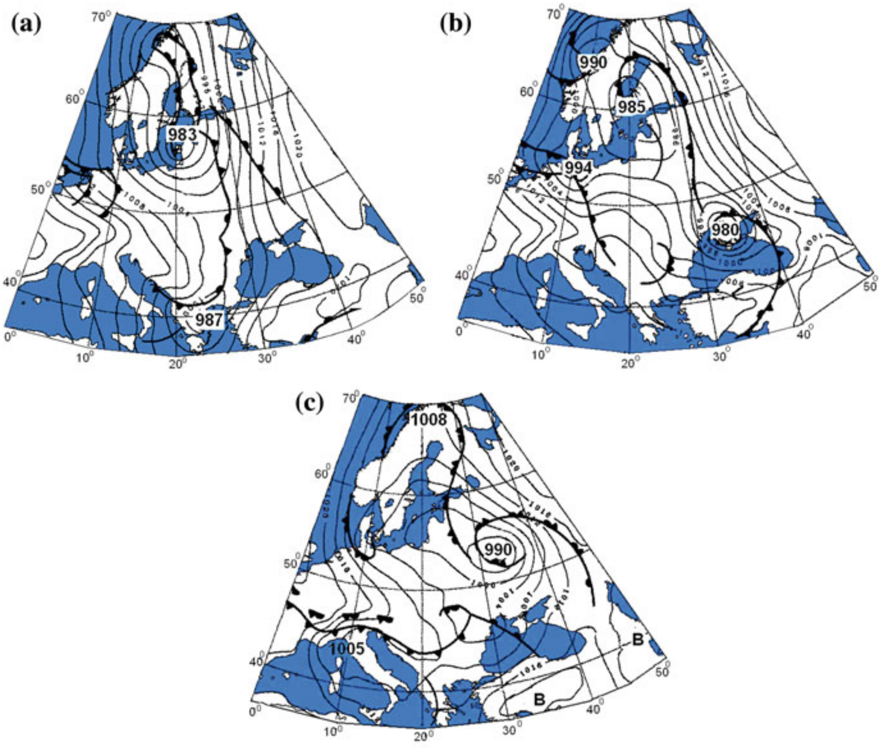


Fig. 8.1 Synoptic situations over the territory of Europe on November 10 (**a**), 11 (**b**), and 12 (**c**), 2007. *Numbers denote pressure, hPa, in the centers of cyclones*

atmospheric pressure in its center fell down to 980 hPa. The horizontal baric gradients sharpened almost over the whole aquatory of the sea that caused strengthening of winds. Off the Crimean coast and over the Sea of Azov they had first the southeast, and then southwest direction. By the morning of November 11 the wind force reached here 20–25 m/s (in Kerch, 27 m/s; in Anapa, 25–30 m/s; in Gelendzhik, 30–35 m/s).

On November 12–13, the cyclone center was displaced from the Crimean Peninsula to the northward (Fig. 8.1c), but the atmospheric trough with rainfall and low cloud persisted over the sea aquatory. On the night of November 12 wind continued to be from the south (13–18 m/s), and on November 13 its direction changed to northwest (7–12 m/s).

On November 14, the zone of increased atmospheric pressure with the SE wind force of 6–11 m/s was observed over the Black and Azov Seas. On November 15, 2007 the next southern cyclone displaced from territory of Italy to Bulgaria, Odessa, and Kharkiv. The most part of the Black and Azov Sea aquatory appeared in its warm sector (8–10°C), with prevalence of the SE–S winds of 8–12 m/s. By data from AMS of Kerch, on November 10–18 wind in the area periodically

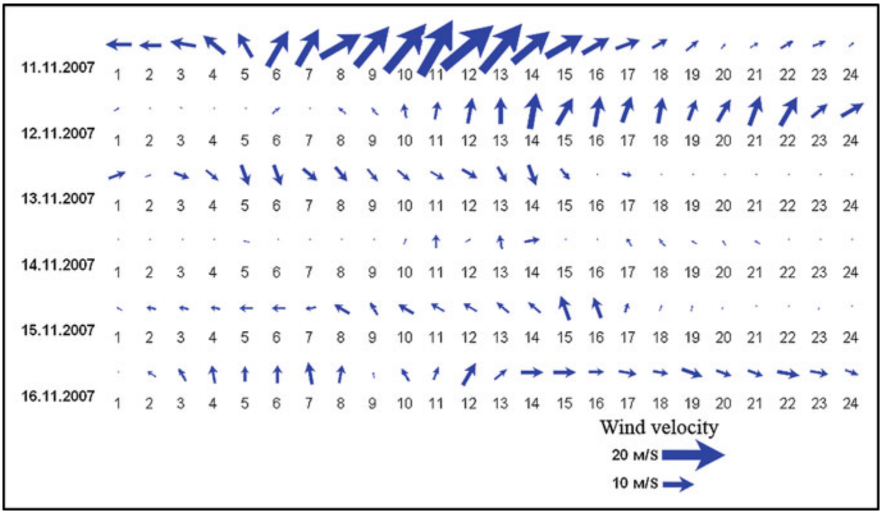


Fig. 8.2 Dynamics of wind force and direction at AMS of Kerch on November 11–16, 2007 by current data (Fashchuk 2009)

changed its direction, weakening to calm and strengthening up to 20 m/s (Fig. 8.2).

On November 16–20, the territory of Ukraine was occupied by atmospheric ridge, while the trough over the Black Sea deepened. With that, the north wind with force of 6–11 m/s changed its direction to northeast, with strengthening up to 12–17 m/s (gusting to 20 m/s). On November 20 the NE wind in Novorossiysk reached 20–25 m/s.

The cyclone passage over the Crimea on November 11 was accompanied by showers, low cloud, and strong wind. According to the report of the Head of the North Caucasian Inter-Regional Territorial Authority on Hydrometeorology and Environmental Monitoring to the Head of Federal Service for Hydrometeorology and Environmental Monitoring dated November 12, 2007, No. 01-12/542, such synoptic situation on the night of November 10/11, 2007 caused strong winds and waves at the coast and on the aquatory of the Sea of Azov:

- from 01:35 to 2:30 a.m. the southeast wind strengthened up to 15–20 m/s;
- from 11:20 a.m. the wind direction changed to southwest, with force of 20 m/s and gusting to 26 m/s;
- in Temryuk, from 02:30 a.m. wind had southeast direction (15–20 m/s); in Yeisk, from 01:35 a.m. the east wind with transition to south (15–22 m/s) was observed, in 9:00 a.m. the wave height was 1 m;
- in Cossack village Dolzhanskaya, from 05:40 a.m. the east wind with transition to southwest (16–22 m/s) was observed; in 9:00 a.m. the wave height was 0.5 m; from 2:51 p.m. wind was from the southwest, its speed reached 13 m/s, and gusting, 26 m/s.

According to the Southern Regional Center of the Ministry of Emergency Situations of Russia, in the Sea of Azov, in the Port Kavkaz area, the wave height was 4 m. At the Black Sea coast, in Anapa, from 02:38 a.m. the south wind with force of 20–25 m/s was observed; at 07:40 a.m. the speed of south wind increased to 25 m/s, with gusting to 30 m/s; at 10:30 its speed was 25 m/s with gusting to 35 m/s. In Novorossiysk, from 02:45 a.m. to 06:00 p.m. wind was from the southeast, with transition to the southwest direction (17–22 m/s); in Gelendzhik, from 02:40 a.m. to 05:00 p.m. there was the southeast wind with transition to southwest (12–15 m/s, gusting to 17–23 m/s), at 04:00 a.m. its speed increased to 25 m/s; in Dzhubga, from 06:20 a.m. the southeast wind with transition to southwest (7–12 m/s, gusting to 18–21 m/s) was observed. The maximum wave height under Novorossiysk was 4 m (Photo 8.1).

In situation observed on November 11–18, 2007, the characteristic of the winter period southwestern type of atmospheric circulation, at which the trough from the Baltic Sea extends to the Balkans and in the process of its deepening the deep cyclones with strong winds are formed over the Black Sea, was realized. The probability of formation of the southwestern type of wind flows in the Kerch Strait area in the period from October to April is 12% (Project “The Seas of the USSR 1991a, b). They usually reach the maximum force (>15 m/s) in the northeastern sea, mainly once a year during the period from November to April. The duration of their influence is on the average 10–13 h (in November, 2007, at AMS of Kerch such wind continued 8 h, see Fig. 8.2).

Storms with the wind speed of more than 20 m/s are observed in the Black Sea, more often, in 1–3% of cases, irrespective of the area and wind direction. The author did not find the data on the stormy south winds such as were observed in November, 2007 in Anapa (S, 25–35 m/s) and Novorossiysk (SE–SW, 17–22 m/s), in any literary sources, including the analysis of winds since 1936.

Photo 8.1 Over the last 50 years waves with the height of 4 m and more were not registered in the Kerch Strait (Photo by author)

The model calculations of wave height in the Black Sea on November 11, 2007, made with the use of wind wave model (Kabatchenko et al. 2001) and confirmed by the above data of current observations in ports, showed that the wave height in the Kerch Strait and in its Black Sea mouth during the storm reached 4–6 m.

The long-term observations at HMS of *Opasnoye* (1954–2002) show (see Table 7.7) that over the last 50 years the maximum wave heights (2 m) in the northern strait were observed only 9 times (6 times in April, 2 times in June, and once in July) under the winds of northern quarter.

It is characteristic that for the 50-year period of observations the high waves, and furthermore the 4-m waves (as it was in the Port Kavkaz and Novorossiysk areas in November, 2007), under the winds of southern quarter in the northeastern sea were never fixed. During the entire year (except for March) waves with height of 0.7–1 m and less (44–51% of cases) prevail in the strait. The occurrence of waves with the height of 1–2 m throughout the year ranges from 1 to 7.3% (Yeremeev et al. 2003).

8.2 Chronicle of the Wreck

According to the Ministry of Emergency Situations of Russia, on the morning of November 11 in the Port Kavkaz area there were 59 vessels, including about 20 oil tank barges of the river-sea type. About the same number of vessels stood at anchorage in the Black Sea mouth of the strait. According to the Captain of the Kerch Port, the total number of vessels on the strait aquatory and in its Azov and Black Sea mouths (in wait for piloting or making cargo transshipment) at that time amounted to 167 units (Fig. 8.3).

The report of the Ministry of Emergency Situations on 06:00 a.m. of November 12, 2007, informed that on November 11, 2007, as a result of stormy wind (up to 32 m/s) and high waves in the sea (force 6–7, wave height of 5 m), 4 vessels (dry-cargo ships *Volnogorsk*, *Nakhichevan*, *Kovel*, and *Hach Izmail* (Georgia)) sank in the Kerch Strait; 6 vessels broke adrift and took the bottom (dry-cargo ships *Vera Voloshinskaya* (Ukraine), *Ziyaya Kos* (Turkey), and *Captain Izmail* (Turkey), barges *Dika* and *Dimetra*, crane vessel *Sevastopolets*); 2 tankers (*Volgoneft-139* and *Volgoneft-123*) were crippled; barge *BT-3754* was on the drift (Fig. 8.4).

The oil tank barge *Volgoneft-139* of the river-sea type transported fuel oil, on 04:50 a.m. of November 11, 2007, broke in two in the anchorage area to the south of the Tuzla Spit Island that resulted in entry of fuel oil into the sea (Photo 8.2). The anchored fore body of the tanker remained on its place (isobath of 10 m), while the stern, under the influence of wind and currents, began to drift towards the Tuzla Island and took here the bottom (the 5-m isobath).

As a result of breakage of the tanker transported 4777 t of fuel oil, there was a spill of about 1300–1600 t of oil products. Moreover, about 6800 t of technologic sulfur contained in holds of other sunken ships appeared on the bottom.

Fig. 8.3 Arrangement of vessels in the Kerch Strait in the period of the wreck in November, 2007 (www.scanex.ru)

8.3 Consequences of the Wreck

There is no exact information about the volume of the spilled fuel oil which got into the sea during the wreck, and its properties. There were suggestions that not only fuel oil from the tanker Volgoneft-139 but oil products from other vessels taken the bottom, which tried to escape the storm, discharging ballast water containing diesel oil and, probably, bunker fuel, came into the sea after the storm. This suggestion was confirmed by the data of air reconnaissance of the accident area, carried out by efforts of the Ministry of Emergency Situations of Russia just after the storm. One way or another, but by the official reports of the Ministry of Emergency Situations after the Volgoneft-139 wreck 600 t of fuel oil flowed out of the fore body of the tanker within 12 h. The beginning of outflow was fixed at 4:50 a.m. on November 11. The outflow of fuel oil from the afterbody which took the bottom near the Tuzla Spit Island, began 3 h later and continued 12 h.

According to the information of Administration of the Kerch Seaport and specialists of the Kerch Division of the Ministry of Emergency Situations of Ukraine (personal communication of the Captain of the Port and Head of the Emergency Response Team), on November 12, 2007, the fuel oil spill “covered” the southern coast of the Tuzla Island (Photo 8.3).

On November 17, fuel oil appeared on the Crimean coast of the strait, in the area of the Arshintsevo Spit and Cape Belyi (Ak-Burun).

Fig. 8.4 Arrangement of sunken vessels in the Kerch Strait after November 11, 2007

Photo 8.2 The grounded stern of the tanker (*Volgoneft-139*), towed to Port Caucasus on 15 November 2007 (www.yuga.ru)

The fuel oil gathering by the Kerch volunteers and specialists of the Ministry of Emergency Situations and Armed Forces of Ukraine on the island beaches and in the specified areas of the strait coast was finished by the end of November, 2007.

Photo 8.3 Spill of fuel oil on the Tuzla Island on November 12, 2007 (Photo by Igor Golubenkov)

On the Cape Belyi up to 500 bags of sand polluted with fuel oil were gathered every day. Its total amount gathered in the Ukrainian territory of the strait was about 4000 t. The fuel oil content in samples of polluted sand ranges from 4 to 30%, being 15–20% on the average. Thus, it may be supposed that from 600 to 800 t of fuel oil were washed up on the Ukrainian coast.

On November 14, 2007, the specialists from the Ministry of Emergency Situations of Russia carried out air reconnaissance (helicopter survey) of oil pollution of the strait and mapping of fuel oil stains on its aquatory and on the coast. 3 days after the wreck, the main fuel oil spills were fixed in the areas of sunken fore body of the tanker Volgoneft-139 and her stern taken the bottom, and also on the coast of the Chushka Spit.

The plume of light ends of oil products with extent of more than 50 km, fixed at the entry into the Kerch Strait from the Sea of Azov, from settlement Kuchugury on the Taman Peninsula along the northern coast of the Kerch Peninsula up to the Kazantip Bay, was associated not with the broken tanker but with those tens of vessels which were in the Sea of Azov at that time and washed out their tanks under the conditions of stormy weather.

On November 15, 2007, the Head of the North Caucasian Territorial Administration for Hydrometeorological and Environmental Monitoring reported that the tow Svetlomor-3 operated in the area of fore body of the tanker Volgoneft-139, gathered 500 m^3 of water and fuel oil mixture. Near the afterbody of this tanker the pumping of fuel oil in the tanker Volgoneft-119 was made. In total, 10 t of fuel oil was pumped out. Also, in the Tuzla Spit area the works on setting of the 400-m oil-spill booms between the spit and the Tuzla Island were conducted. About 1 t of sorbent was applied in the area of the Tuzla Island and fore body of the tanker Volgoneft-139.

On November 14, 8.5 km of the Russian shore were cleaned out from fuel oil; 1478.6 t of polluted sand were collected, and, in total, 3248 t of this sand were gathered from the beginning of cleaning operation. Supposing the content of fuel oil in polluted sand on the Russian coast is the same as on the Ukrainian Coast, it turns out that the sea “presented” Russia up to 600 t of oil products. Together with the Ukrainian fuel oil it makes 1400 t, i.e. almost the whole volume of oil products which got into the sea after the wreck!

The most of experts, who analyze the causes and consequences of the wreck on November 11, 2007, believe that its real scales (volume of the spill) are underestimated, and up to 500 t of fuel oil still remain on the Kerch Strait bottom.

8.3.1 Aquatory and Coast of the Strait in the First Days After the Wreck

The extreme November storm in the Kerch Strait continued from 5 a.m. to 2 p.m. of November 11, 2007. As early as 9 a.m. of November 12, the diving boat of the Ministry of Emergency Situations of Ukraine surveyed the Tuzla Island coast, and by 2 p.m., the strait aquatory in the area of the sunken vessels (Photo 8.4).

By the results of inspection, the drifting stains of fuel oil from the tanker *Volgoneft-139* were not revealed visually. Individual lumps of fuel oil were noted against the sea surface covered with film of light ends of oil (diesel fuel), which got into the sea from tanks of three other ships sunken in the strait, *Nakhichevan*, *Volnogorsk*, and *Kovel* (Photo 8.5).

In November–December, from 5–7 to 50,000 birds of more than 40 species congregate traditionally in the Kerch Strait, bays and limans of the Taman Peninsula for wintering. As a result of fuel oil spill, waterfowl and shore species, such as coot, great crested grebe, red-necked grebe, black-necked grebe, little grebe, cormorants, suffered most of all (Photo 8.6). Their kill was associated with overwarming of body and gluing of plumage as a result of direct contact with fuel oil.

In February, 2008 the wave of wintering birds kill has returned. It took the species feeding on sea grass polluted with fuel oil and zoobenthos, including common teal, red-duck, Caspian gull, rock pigeon, black-throated loon, and single individuals of swan, pheasant, and wild duck. By December 12, 2007, more than 5000 dead birds were collected on the Taman Peninsula coast, and their total number was about 12000 individuals. With that, about 3000 birds remained alive but to a different extent polluted.

8.4 Prognosis of Probable Oil Spill Dynamics in the Kerch Strait

The reconstruction of oil spill dynamics under the influence of hydrometeorological factors, realized on the Russian hydrodynamic model SPILLMOD, has described the current situation with the Kerch Strait pollution after the wreck rather adequately (after its comparison with the air recognaissance data) (Ovsienko

Photo 8.4 Dry-cargo ship of the river-sea type similar to the dry-cargo ship *Kovel* (*top*) and deck-house (*bottom*) over the Kerch Strait surface after its wreck on November 11, 2007 (Photo by Sh. Mosharipov)

et al. 2008). According to model calculations, within 4 days after the wreck the considerable part of the strait aquatory and the Azov near-strait area were in the zone of fuel oil stain (Fig. 8.5).

Fuel oil is a liquid product of dark brown color, the residue after separation of gasoline, kerosene, and gasoil cuts distilled at 350–360°C, from oil. It represents a mixture of hydrocarbons, petroleum resins, asphaltenes, carbenes, carboides, and the organic compounds containing metals (V, Ni, Fe, Mg, Na, Ca). The physicochemical properties of fuel oil depend on chemical composition of crude oil and degree of recovery of distillate fractions and are characterized by the following parameters: viscosity of 8–80 mm^2/s (at 100°C), density of 0.89–1.015 g/cm^3 (at 20°C), setting point of 10–40°C.

Photo 8.5 Individual lumps of fuel oil (*top*) and oil slicks (*bottom*) on the Kerch Strait surface after the wrecks on November 11, 2007 (Photo by Sh. Mosharipov)

By its density fuel oil is divided into four categories: M-100/1015, M-100/1010, M-100/1000, and M-100/985. The numbers in denominator represent density of fuel oil (kg/m^3) at temperature of 20°C. The author has no the information about the density of oil products transported by the tanker Volgoneft-139. At the same time, the diagrams of its changes within the range from 0 to 25°C and from 10 to 20‰ constructed on the basis of the revealed relationship of fuel oil density with water temperature and salinity are available (Manovyan 2001).

After superimposition of these diagrams for various grades of fuel oil and graphs of water density changes in the Kerch Strait within real for this area temperature (1–24°C) and salinity (11–18.4‰) ranges, it became obvious that if the tanker Volgoneft-139 transported fuel of the M-100/1015 grade, under the real variations of temperature and salinity in the Kerch Strait it could not rise to the surface with an increase in water temperature because warming of water and fuel oil occurred synchronously, and the latter remained denser than water even at 25°C. The surfacing of such fuel oil is possible only in unreal situation when it warms up to 22–25°C, while the water temperature remains in the range of 0–7°C (Fig. 8.6).

In case, the tanks of the broken tanker contained fuel oil of the M-100/1000 or M-100/985 grades, all oil products after the wreck had to appear on the surface,

Photo 8.6 On the Russian coast of the Kerch Strait populations of *great crested grebe* (*top*—by I.Kudrik)) and great cormorant (bottom—by I. Torgachkin) suffered from oil spill most of all

as even at zero temperature such fuel oil is lighter than water. It also could be seen on the sea surface, if the Volgoneft-139 transported fuel oil of the M-100/1010 grade, but for this water salinity had to exceed 15‰, and temperature, 17°C. Indeed, in these situations almost the whole spill (1600 t) could be washed up on the strait beaches after the storm.

The fate of fuel oil gravitated to the strait bottom can be predicted from the estimations of prevailing wind directions over the strait, direction and velocities of currents in the spring-summer months presented in the geographic and ecological information model (see Chap. 7), and also from data on the character of oil product transformation in sea water (Patin 2001).

From the geographic and ecological model of the Kerch Strait it follows that the wind activity over its aquatory and physiographic features of the Sea of Azov determine the fact that its water exchange with the Black Sea occurs by means of reciprocating motions developing due to the level difference between its northern (Azov) and southern (Black Sea) parts, across the whole section of the strait (see Sects. 7.4.1–7.4.2).

The construction of the Tuzla dam changed also the circulation structure in the strait. Under the south winds Black Sea waters began to flow into the Taman Bay

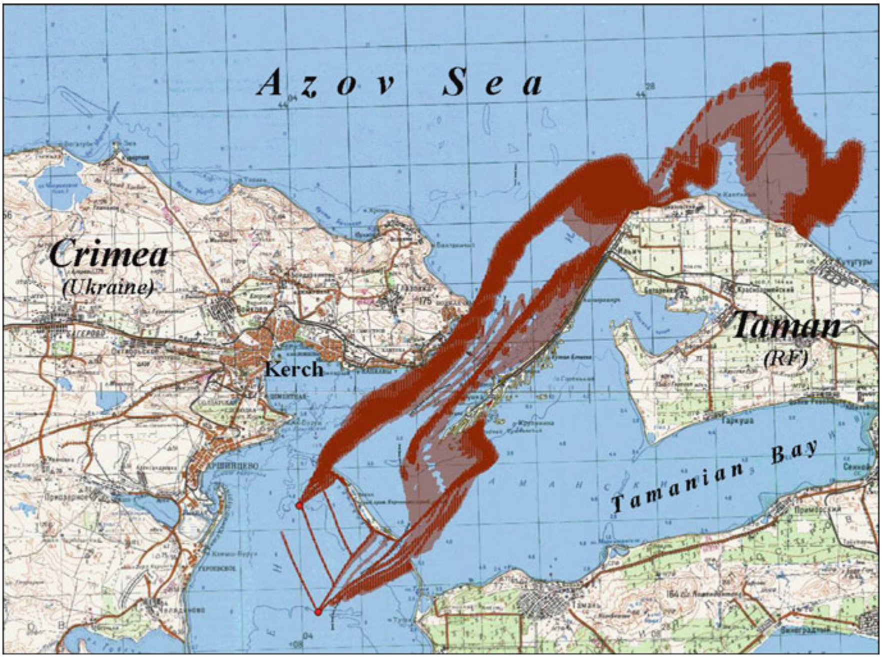


Fig. 8.5 Aquatory of the Kerch Strait turned out to be under the influence of fuel oil spill from the tanker Volgoneft-139 on November 11–15, 2007, by results of mathematical modeling (Ovsienko et al. 2008)

not through the Tuzla channel but via the section along the strait (Tuzla Island–Chushka Spit) only after the passage of the Pavlovskaya Narrow. As a result, during these periods the cyclonic type of circulation in the bay (counterclockwise) was replaced by the opposite, anticyclonic, type favoring accumulation of suspended particles in the bay and, correspondingly, its silting. Moreover, unfinished dam became the barrier for Black Sea waters and favored, under the south winds, development of the southern counter-current flow along the Taman coast and local anticyclonic circulation in the southern strait from the Black Sea side of the dam (see Fig. 7.9, right).

On November 11, 2007, under the influence of stormy southwest wind Black Sea waters penetrated into the strait zone up to Port Kavkaz. The salinity here amounted to 17.7‰ (Matishov et al. 2008a, b). Under such salinity (see Fig. 8.6) fuel oil of the M-100/1010 grade had neutral buoyancy and it is quite probable that the major part of its spill was washed out on the Tuzla Island and Chushka Spit beaches by the storm. Fuel oil remained in water and driven by the storm into the Sea of Azov, started to sink and gravitate to the bottom, because at sea water salinity of 12–13‰ it became heavier than water (see Fig. 8.6). After the storm termination on November 14–19, the compensatory Azov current restored after the storm surge, "returned" the rests of the sunken fuel oil from the Sea of Azov to the

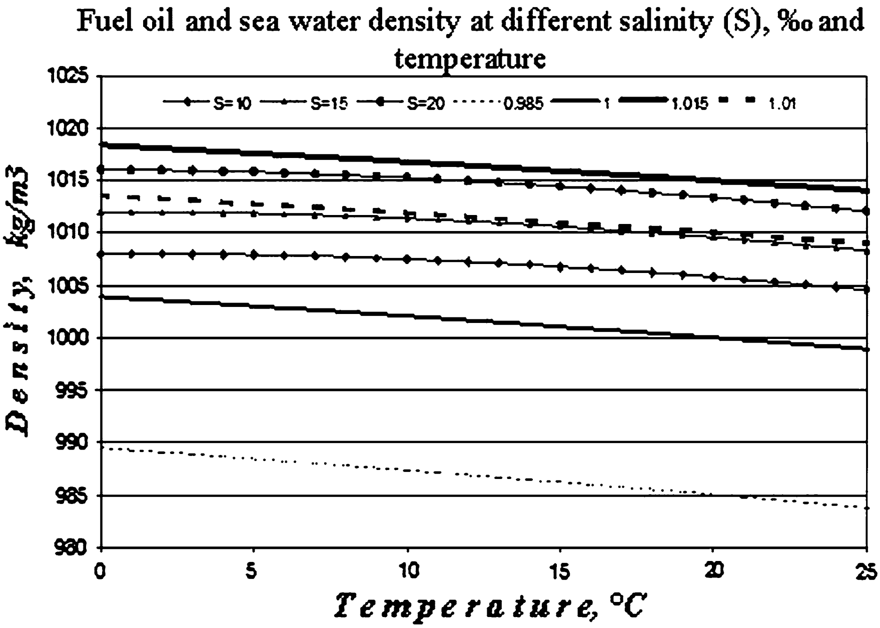


Fig. 8.6 Dependence of density of sea water with different salinity and fuel oil of various grades (with different initial density) on temperature (Ovsienko et al. 2008)

Kerch Strait along its Crimean coast, despite the low wind weather (see Fig. 8.2). With that, its appearance on the coast was observed on the beaked sites of the Ukrainian coast, on Cape Ak-Burun and the Arshintsevo Spit.

Being a mixture of heavy fractions f hydrocarbons, fuel oil can remain in sea water for a rather long time without essential transformation. Its lumps, oil aggregates with size from 1 mm to 50 cm, “live” in the interior seas from 1 month to 1 year, and in the open ocean, up to several years. They consist mainly of *asphaltenes* (*50%*), high molecular weight compounds of heavy oil fractions.

At rising of such oil aggregates to the surface in the open part of the Kerch Strait aquatory, between the Chushka Spit, Tuzla Island and the Crimean coast, after the storms, with a probability of about 60% (a share of the Azov currents in the strait for a month) within one day they will be taken out to the Black Sea, and the probability of their washing out on the coast is the highest along the coastline from Kerch to exit from the strait into the Black Sea (the Arshintsevo Spit, settlements Geroevskoye and Zavetnoye, Cape Takil).

With a probability of 35% (a share of the Black Sea currents) oil aggregates, rising to the surface after the storms, will be transported into the Sea of Azov, touching the Chushka Spit coast, settlements Kapkany, Opasnoye, Zhukovka, and the Kerch Bay, and in 6% of cases (a share of the combined currents for a month) the fate of oil aggregates seems uncertain.

It is much more difficult to estimate the development of situation concerning the Taman Bay pollution with fuel oil lumps during the spring-summer period, in case of their rising to the surface after aggregation of fuel oil. Taking into account the weakening of its water exchange with the open strait aquatory after construction of the Tuzla dam and change of the character of water circulation to the anticyclonic type (with accumulating effect), the probability of long retention of oil aggregates, from which the strait will not clear by a natural way, i.e. without application of technique, is high.

8.5 The Kerch Strait: A Year After the Wreck

In 2007–2008, about 10 organizations were engaged in an estimation of the consequences of the stated wreck in the Kerch Strait. We tried to present this process chronologically and sum up the results of independent research (Fashchuk et al. 2009, 2010a, b).

8.5.1 *Research Conducted by the Organizations of the Federal Service for Hydrometeorology and Environmental Monitoring*

The next day after the Kerch catastrophe, the specialists from the Kuban Estuarine Hydrometeorological Station (Temryuk) of the Krasnodar Regional Center for Hydrometeorology and Environmental Monitoring organized the coastal control of oil pollution of the coastal waters and bottom sediments. For this purpose, in 2007–2008 (13 months), the inspection of the Black Sea coast, the Kerch Strait, the Taman Bay, and the Sea of Azov, from Anapa to Zozulievskoye Girlo and Sladkovskoye Girlo was carried out. In the course of this inspection, the samples for relevant analyses were taken at 20 points near the coast at depth of 0.5 m (Fig. 8.7).

The first inspection of the coastal zone was made on *November 12–15, 2007* (Fashchuk et al. 2010a, b). Within a month after the wreck, the samples were taken every 3 days. At the end of the yearly period, due to the stabilization of the situation, they were taken once a month.

For the whole period of observations (13 months) the highest concentration of oil products in water, 2.500 mg/L (50 MACs), was fixed on November 12 on the Chushka Spit, at a distance of 4 km northeast of Port Kavkaz (Table 8.1).

Under the influence of the southwest winds (18–32 m/s) observed during the storm on November 11–13, the oil pollution extended rapidly from the strait to the Sea of Azov. Already on November 13, in the Port Kavkaz area the oil product concentration in water decreased from 2.5 to 1.736 mg/L (34.7 MACs), while

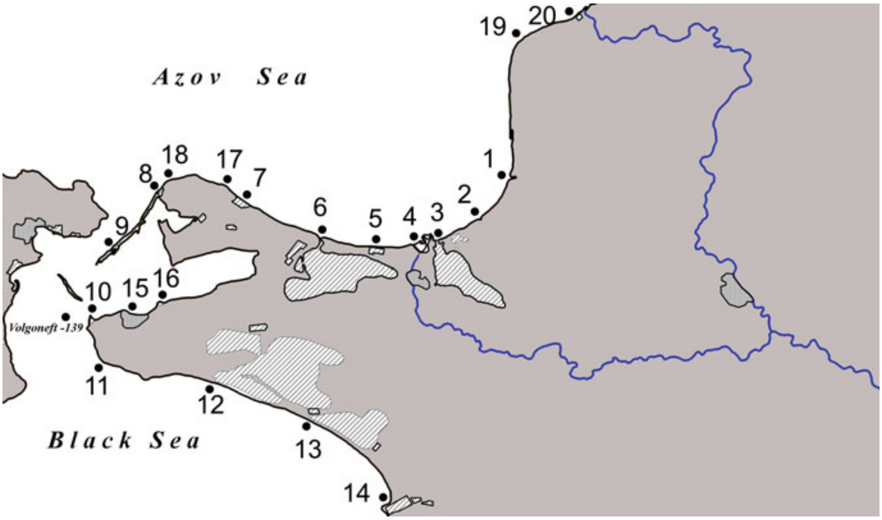


Fig. 8.7 Areas of the coastal research conducted by the Krasnodar Regional Center for Hydrometeorology and Environmental Monitoring for assessment of the Kerch catastrophe consequences (Fashchuk et al. 2010a, b). 88 *Locations: 1—Zozulievskoye Girlo, 2—Kulikovskoye Girlo*, *3—Soloviyovskoye Girlo,4—Port Temryuk*, *5—Golubitskaya*, *6—Peresyp*, *7—Kuchugury*, *8—settlement Iliych*, *9—Port Kavkaz*, *10—Tuzla Spit*, *11—Cape Panagiya*, *12—settlement Vesyolovka*, *13—Blagoveshchenskaya*, *14—Anapa*, *15—Taman*, *16—settlement Primorskyi*, *17—Cape Pekly*, *18—Cape Achilleon*, *19—Gorkovskoye Girlo*, *20—Sladkovskoye Girlo*

Table 8.1 Content of oil products in coastal waters of the Kerch Strait and the Sea of Azov after the Kerch catastrophe by results of observations conducted by structural divisions of the Federal Service for Hydrometeorology and Environmental Monitoring (Fashchuk et al. 2010a)

Aquatory	Location	Date	Concentration, mg/L	Units of MAC
Kerch Strait	Chushka Spit—4 km northeast of Port Kavkaz	12 Nov 2007	2.500	50.0
	End of the Tuzla dam—left coast	13 Nov 2007	0.269	5.4
	End of the Tuzla dam—right coast		0.193	3.9
	Head of the Tuzla dam—left coast		0.343	6.9
	Port Kavkaz		1.736	34.7
Northern mouth of the strait	settlement Iliych	15 Nov 2007	0.640	12.8
Sea of Azov	settlement Kuchugury		0.64	12.8
	settlement Za Rodinu		0.09	1.8
	settlement Peresyp		0.47	9.4
	Cossack village Golubitskaya		0.04	0.8
Taman Bay	Cossack village Zaporozhskaya		0.55	11.0
	settlement Primorskyi		0.55	11.0

along the Azov coast, at distance of 35–40 km from the Kerch Strait, it increased up to 9–13 MACs. Off the Black Sea coast the pollution made only 3.9–6.9 MACs. Hereafter, with transition of winds to the western bearings, the oil pollution began to spread into the Black Sea; on November 16, the oil product concentration in the area of settlement Volna was 16 MACs. However, the polluted waters did not reach Anapa. Their eastern boundary was located near the western forepart of the Bugazskaya Spit (settlement Vesyolovka, 30 km from the sunken tanker). The maximum water content of oil products was registered here on November 18 (4.2 MACs), but already on November 22 it decreased to 0.6 MAC and then remained within 0.2–0.8 MAC, increasing to 1.0–1.8 MACs only sometimes.

During the spring-summer season, 2008, the content of oil products in coastal waters of the strait did not exceed 2–4 MACs, and from the mid-October, 2008, the situation in the coastal zone of the territorial waters of Russia in the Kerch Strait, Black and Azov Seas was stabilized; the water pollution level was mainly 0.5–0.9 MAC (Fig. 8.8).

The oil pollution of beach deposits was found to be vertically inhomogeneous. The maximum concentrations of oil products were fixed on the beaches of settlement Peresyp in the layer of 10–15 cm (0.22 mg/g of dry weight) and on the Tuzla dam in the layer of 5–10 cm (0.65 mg/g of dry weight) that was 4.4 and 13 times higher than the background concentrations, not exceeding 0.02–0.05 mg/g of dry weight.

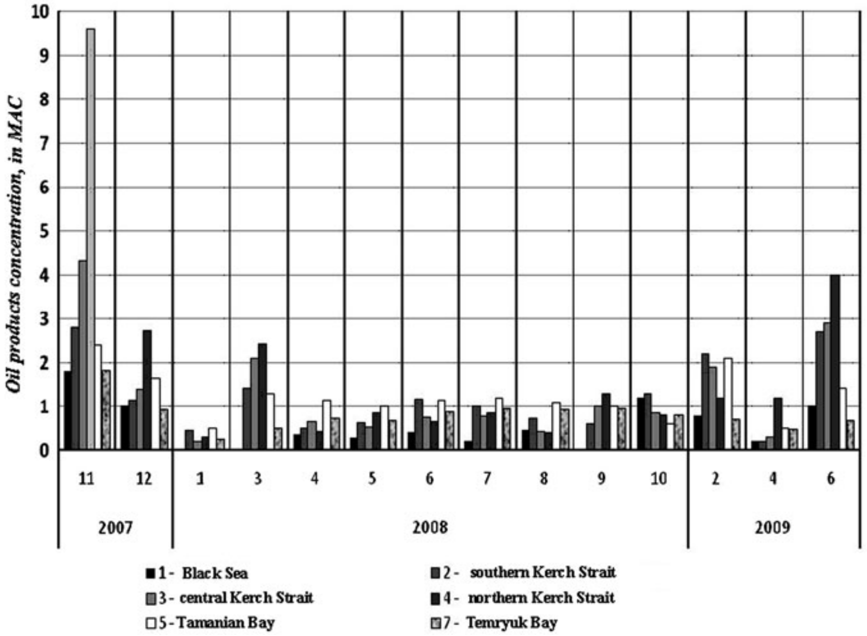


Fig. 8.8 Mean monthly OHC content (in MACs) from November 2007 to February 2009 by the Kerch Strait areas (Korshenko and Panova 2009)

8.5.2 Research Conducted by the Azov Research Institute of Fisheries (AzNIRKH)

Two days after the wreck, *on November 13–17, 2007*, the specialists from the FSUE *AzNIRKH*, together with the representatives from the Azov-Black Sea Territorial Administration of the Russian Federal Fisheries Agency and the Temryuk Interdistrict Department of the FSI *AzCherrybvod*, surveyed the seashore sites from Cape Zhelezny Rog-Cape Panagiya in the Black sea to Cape Achilleon–Cossack village Golubitskay in the Sea of Azov (The Kerch wreck: consequences for aquatic ecosystems 2008). At 18 points of the coast, the water and ground samples were taken for analyses on the oil product content (Fig. 8.9).

The fuel oil stains with size from 1 to 15 m^2 and thickness of 1–5 cm were fixed in the most part of the surveyed coast. The width of the polluted seashore on the Tuzla Spit ranged from 1 to 10–12 m, and its extent was 4.5 km. Along the entire coast of the Chushka Spit the concentration of oil products varied from 2.06 to 156 mg/L (26–3120 MACs). In the Tuzla Spit area this characteristic ranged from 7.36 to 22.62 mg/L (147–452 MACs); in the Sea of Azov, at Cape Kamennyi, it amounted to 29.8 MACs; and in the Temryuk Bay, in the area of settlement Kuchugury, the concentration of oil products in water reached the extreme value of 707 mg/L, or 14140 MACs (Table 8.2).

Twenty days after the wreck, from *November 30 to December 7*, AzNIRH carried out the second expedition in the Kerch Strait (11 stations) and adjacent aquatories of the Black (7 stations) and Azov (20 stations) Seas. *In the Kerch Strait*

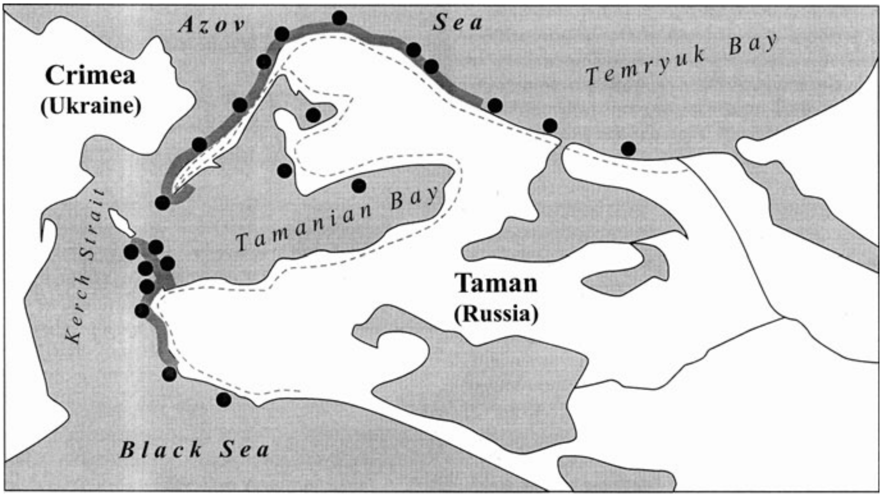


Fig. 8.9 The scheme of stations for monitoring of the Kerch wreck consequences, conducted by AzNIRKH on November 13–17, 2007 (The Kerch wreck: consequences for aquatic ecosystems 2008). *Thick line confines the zone of seashore pollution with fuel oil*

Table 8.2 The content of total oil products in coastal waters of the Kerch Strait and the Sea of Azov on November 13–17, 2007, by the AzNIRKH data (The Kerch wreck: consequences for aquatic ecosystems 2008)

Aquatory	Locations of sampling	Concentration (mg/L)	Units of MAC
Sea of Azov	Cape Kamennyi	1.49	29.8
	settlement Kuchugury	707.0	14140
		0.09	1.8
	settlement Peresyp	0.04	0.8
Kerch Strait	settlement Iliych	0.47	5.4
	Chushka Spit	156.0	3120
		2.06	41.2
		1.30	26
		1.64	32.8
	Tuzla Spit (southwestern side)	0.21	4.2
		0.22	4.4
		0.16	3.2
	Tuzla Spit (northeastern side)	15.58	311.6
		7.36	147
		22.62	452
	Cape Tuzla	0.07	1.4

waters, the concentrations of oil products ranged from 0.02 to 0.34 mg/L (0.4–6.8 MACs).

In bottom sediments of the Kerch Strait the content of oil products varied from 0.02 to 0.33 mg/g of dry weight, averaging 0.16 mg/g of dry weight, that practically coincided with the data obtained by the Krasnodar Regional Center for Hydrometeorology and Environmental Monitoring.

The MAC for oil products was exceeded *in Azov Sea waters* at 41% of stations, with the maximum of 3.4 MACs. The content of oil products *in bottom sediments of the Sea of Azov* ranged from 0.06 to 0.45 mg/g of dry weight, averaging 0.26 mg/g.

8.5.3 Research Conducted by the Southern Scientific Center of the Russian Academy of Sciences

In the period from November 2007 to February 2008, the Southern Scientific Center of the Russian Academy of Sciences conducted eight ecological expeditions in the Kerch wreck area. *From November 15–19*, 80 km of the strait coast, from Cape Tuzla to settlement Kuchugury, were surveyed with the water and ground sampling at 23 stations in the strait (area of the Tuzla and Chushka Spits) and in the Taman Bay (Fig. 8.10, top).

From December 11 to December 19, the second expedition with similar research at 35 stations covered also the southern part of the Russian coast of the Kerch Strait was carried out (Fig. 8.10, bottom).

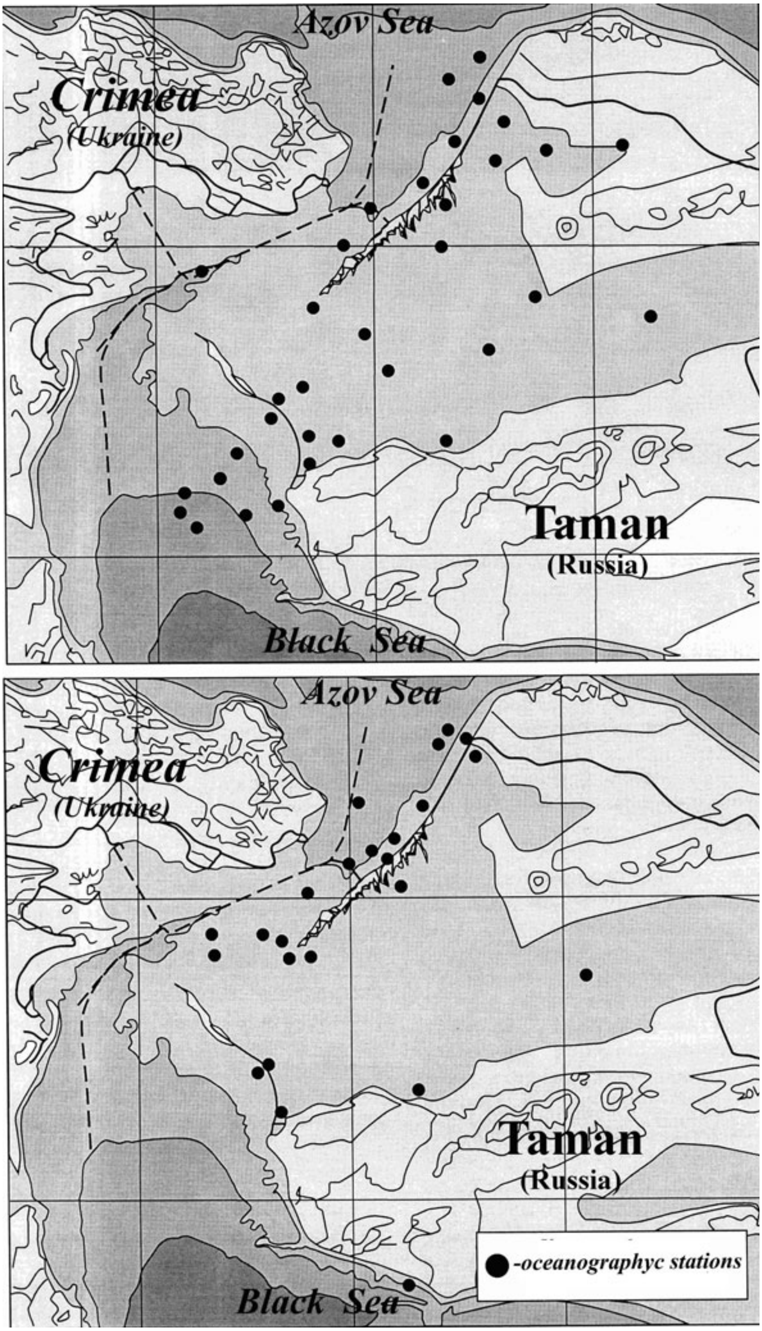


Fig. 8.10 The scheme of stations for monitoring of the Kerch wreck consequences, conducted by the Southern Scientific Center of the Russian Academy of Sciences on November 15–19 (*top*) and December 11–16 (*bottom*), 2007. (Matishov et al. 2008a). (*Dashed line—Kerch-Yenikalian Channel*)

At the same period (*November 14–December 25*), the monitoring of water and bottom sediment pollution level in the strait was conducted by specialists from the Kuban Basin Water Administration (Matishov et al. 2008a, b; http://www.kbvu-fgu.ru).

On November 15–19, the sea surface in the open part of the strait was covered by small single clusters of fuel oil mixed up with seaweed. With approaching the coast, in the area of the middle Chushka Spit, fuel oil and seaweed bunched forming continuous strips which drifted along the coastal line. When taking the samples of bottom sediments, pure fuel oil was found in the channel between the Tuzla Island and Tuzla Spit, and off the tip of the Chushka Spit. The content of oil hydrocarbons in the Kerch Strait at this time varied from 0.03 to 0.94 mg/L (0.6–18.8 MACs), but already by the end of December the water content of oil products in the investigated strait area did not exceed the MAC.

8.5.4 Studies Conducted by the Southern Research Institute of Fisheries and Oceanography (YugNIRO)

Ten days after the wreck, *on November 21*, *2007*, the specialists from the Laboratory of Marine Ecosystem Protection of YugNIRO carried out the monitoring of oil pollution of the waters and bottom sediments in the area of the sunken ships and at three background stations in the catastrophe area, which continued until May, 2008 (Petrenko et al. 2008).

In November, the water content of oil products around the Tuzla Island did not exceed the MAC, but in bottom sediments the value of this characteristic was very high, 0.493–2.024 mg/g of dry weight. The maximum concentration of oil products in bottom sediments was observed in the area of the sunken fore body of the tanker *Volgoneft-139*. Near the dry-cargo ship *Nakhichevan* the value of this characteristic was 1.897 mg/g of dry weight, and at the buoy No.27, 1.393 mg/g of the dry weight. In the rest of the strait aquatory the concentration of oil products in sediments did not exceed 1 mg/g of dry weight, the value above which the changes in bottom organisms become apparent (Mironov et al. 1986).

Three months after the wreck, *on February 07*, *2008*, the water total content of oil products, remaining within the MAC, decreased 1.3 times, and the concentrations of their heavy fractions, 4.2 times. However, there was a redistribution of bottom sediment pollution: near the afterbody of the tanker *Volgoneft-139* (western coast of the Tuzla Island) the concentration of total oil products increased up to 2.988 mg/g of dry weight (Fig. 8.11); at the buoy No. 27, to 2.406 mg/g; while near the sunken fore body of the tanker it decreased to 1.225 mg/g of dry weight. The content of heavy fractions also considerably reduced, from 7–40% (in November) to 2–4%.

By *April 22*, *2008*, the level of water pollution in the area under investigation raised essentially. The maximum concentration of oil products was fixed around the buoy No. 27, 0.128 mg/L (2.6 MACs) on the surface and 0.219 mg/L

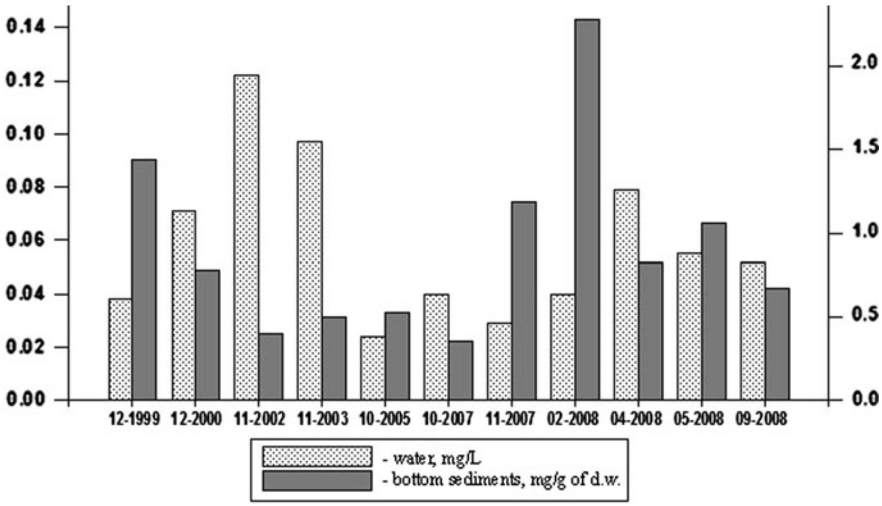


Fig. 8.11 Oil product concentrations in water and bottom sediments in the area of inner road transshipments for 1999–2008 (Petrenko et al. 2008)

(4.4 MACs) in the near-bottom layer. The content of almost untransformed fractions in water increased 7 times, while in bottom sediments it decreased almost the same number of times. The similar situation was observed near the tanker *Volgoneft-139*; the water concentrations of oil products increased by a factor of 1.5–2, while in bottom sediments they reduced 2 (fore body) and 8 (stern) times.

In *May*, *2008*, the maximum water concentration of hydrocarbons (1.8 MACs) was noted in the central part of the strait. Decreasing southwestward to 0.6 MAC, this characteristic in bottom sediments varied from 0.568 to 1.188 mg/g of dry weight, with the maximum near the sunken fore body of the tanker *Volgoneft-139*.

8.5.5 Research Conducted by the Institute of Oceanology of the Russian Academy of Sciences and the World Wild Life Fund

From February 26 to March 12, *2008*, the Institute of Oceanology of the Russian Academy of Sciences and the World Wildlife Fund conducted the joint expedition to the Taman seashore of the Kerch Strait. Its objectives include: visual estimation of coastal oil pollution; determination of the oil pollution level of bottom sediments; determination of the oil product content in bottom organisms; assessment of biodiversity of bottom communities in typical marine biotopes for further monitoring of their changes; determination of physiological condition of bottom animals (bivalves) for estimation of oil product impact on them. 39 stations with diving and sampling in the coastal zone were made from the rubber boat. In total, 34 specimens of bottom sediments, 66 samples of macrozoobenthos, 33 samples of hydrobionts for determination of their contamination level (26 samples of animals and 7 samples of plants), and 8 samples of mollusks for the analysis of their physiological condition were taken. Moreover, 15 descriptions of bottom vegetation were made (Kolyuchkina et al. 2009).

The investigations covered the coasts of the Chushka and Tuzla Spits, part of the Azov Sea coast from settlement Iliych to settlement Kuchugury, the Dinskoy and Taman Bays. As a result, it was established that the offshore coastal zone and bottom of the coastal areas of the Chushka and Tuzla Spits were most affected by fuel which got into the sea, The fuel oil accumulation occurred also on the bottom of the Taman Bay. The visual diving inspection of these areas showed the existence of extensive bottom areas here, covered by a layer of recent fuel oil from the tanker.

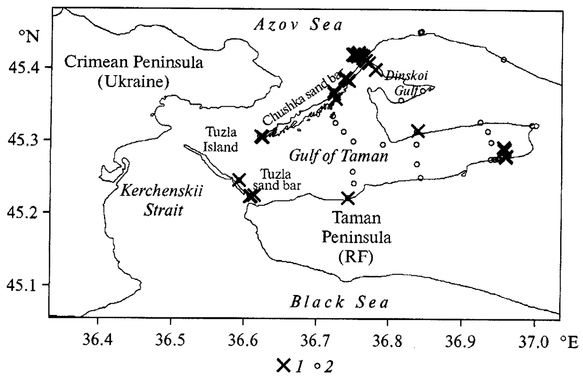
The oil product concentrations in sediments ranged from 9 to 1106 mg/kg that was by 1–2 orders higher than the geochemical background value in bottom sediments of the White, Kara, and Pechora Seas, not subject to the strong anthropogenic contamination. By its maximum value this characteristic was 13–35 times higher than that fixed by the specialists from the Kuban Basin Water Administration on December 14–25, 2007, in the northern Kerch Strait from the Tuzla Island to the Sea of Azov (http://www.kbvu-fgu.ru) and in the Kerch Strait during the 1999–2005 period (30–80 mg/kg) (Klenkin et al. 2007). The similar concentrations (to 1 mg/kg, and up to 3–5 mg/kg by the maximum) were determined by the specialists from the Southern Research Institute of Fisheries and Oceanography (YugNIRO), Kerch, in the Karkinit Bay, in the area of the offshore gas production on the northwestern shelf of the Black Sea (see Fig. 5.15c). The stations located at the eastern coast of the Chushka Spit, in the Dinskoy Bay near settlement Iliych, at the southern tip of the Chushka Spit, and in the inner part of the Taman Bay were the most polluted (http://www.sea.gov.ua).

According to the conclusion of the report's authors (http://www.wwf.ru), there were the fragmentation of fuel oil spill, its local settlement to the bottom, and accumulation in mud sediments and aquatic vegetation in the surveyed water areas. The content of oil products in sea water varied from 0.27 to 1.07 mg/L, exceeding the MAC by a factor of 5.4–21.4. It was somewhat higher, compared to the values fixed here just after the tanker wreck in November 2007 (up to 0.94 mg/L) and 5–20 times higher than one month after the wreck, in December 2007 (Matishov et al. 2008a, b).

On July 16–31, *2008*, the summer expedition conducted by the Institute of Oceanology of the Russian Academy of Sciences in the Kerch Strait, made 39 stations which covered the coasts of the Chushka and Tuzla Spits, the part of the Azov Sea coast between settlements Iliych and Kuchugury, the Dinskoy and Taman Bays (Fig. 8.12).

The visual observations on the coastal (at 18 stations) and bottom (at 21 stations) pollution with fuel oil were carried out. 36 samples of sediments and 30 samples of near-bottom water were taken for further analysis on their hydrocarbon content. Many stations made during the first expedition in February–March, were

Fig. 8.12 The scheme of expedition investigations stations of the Kerch Strait seashore and Russian territorial waters, conducted by the Institute of Oceanology of the Russian Academy of Sciences on 2008 (Kolyuchkina et al. 2009)—(*1—stations carried out from February 26 to March 14*; *2—expedition of July 16–31*)



repeated in the summer. The summer research showed a practically complete absence of visual fuel oil traces on the investigated aquatories and on the coast where in spring, the maxima of oil pollution both in bottom sediments and sea water were observed.

Nevertheless, the fact of anthropogenic pollution of bottom sediments by hydrocarbons in the area under investigation was confirmed by the presence of significant "peaks" of naphtheno-aromatic compounds in the spectra of chromatograms, with the maxima in the area of C_{18} and $C_{27–30}$ (Belyaev et al. 2009).

The height and shape of "peaks" in the spectra show the degree of organic matter biodegradation in sediments. The oil product pollution was observed to a greater or lesser extent in all analyzed samples. The total concentrations of oil hydrocarbons in bottom sediments during the summer period, 2008, ranged from 4.9 to 2946 µg/g, and the content of normal alkanes, from 0.03 to 17.3 µg/g of air-dry weight.

The mean hydrocarbons concentration, equaled to 2.45 µg/g, was considerably higher comparing with background. GC-analysis of aliphatic hydrocarbons in the bottom sediments indicate the presence of *four types* of hydrocarbons in organic matter (OM): (1) mixed terrigenous-planktonogenous origin without pollution OM, (2) the main part of aliphatic hydrocarbons was generated of OM degradation, (3) mixed matter of natural origin with the traces of oil pollution, and (4) highly oil-products polluted OM.

The main part of oil polluted places had the similar characteristics. There were separated and apex parts of Dinskoj and Tamanskij bays with low water dynamic and reducing conditions of sedimentation, which stopped destruction of OM input. Also the higher and maximum concentrations of hydrocarbons were detected in samples from stations with heightened anthropogenic press. Detailed analysis of bottom sediments samples indicated the presence of pollution, undergone intensive processes of biodegradation and resedimentation, in most of the examined sites. Authors could not clearly say that oil spill is source of this pollution. The results of present studies are insufficiently to reveal black oil spill hydrocarbons from background chronic anthropogenic pollution of region. This question should be answered by started already analysis of polyaromatic hydrocarbons fraction.

The most of anthropogenic polluted places characterized by debris deposition, so black oil pollution can concentrate at such areas.

8.5.6 Research Conducted During the UNEP Expedition

The expedition conducted by the European Commission on the United Nations Environment Programme (UNEP) worked in the coastal waters and the area of the Ukrainian Coast of the Kerch Strait *from July 15 to July 25* (Oil Spill in the Kerch Strait 2008). Six samples of bottom sediments were taken in the coastal waters, at the waterway of the Kerch-Yenikalian channel and around the Tuzla Island at depths of 2–8 m (Fig. 8.13).

On the beaches of the coast from Cape Kazantip to settlement Zavetnoye (the southern part of the strait) 12 sand samples with grass were taken for determination of the oil product content. The heavy fractions of oil products, naphthenes and paraffins, prevailed (80–90%) in all samples. In the coastal samples of bottom deposits their concentrations were 42–110 mg/kg of deposits, and at the stations 14–17 located near the sunken fore body of the tanker *Volgoneft-139* the content of oil products in deposits increased to 300–600 mg/kg. The pure fuel oil also was not detected on the bottom of the area under investigation.

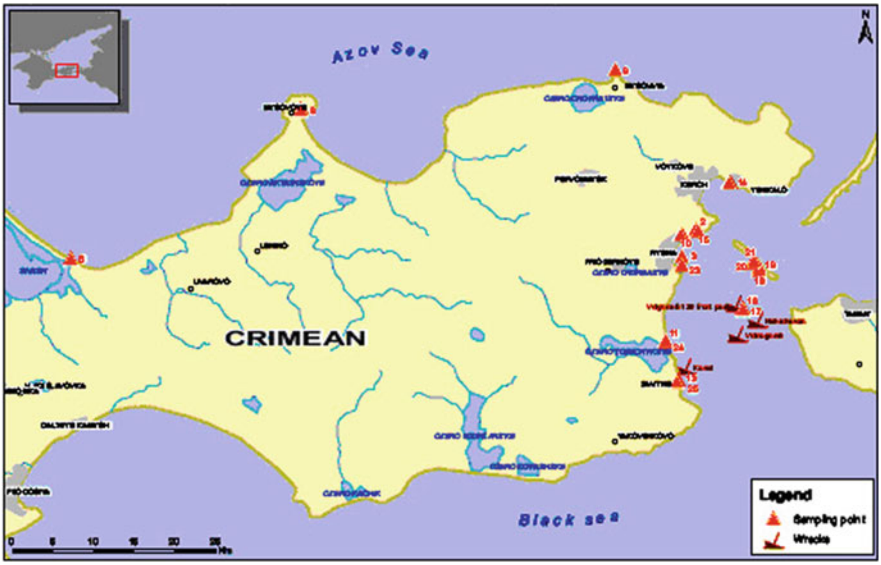


Fig. 8.13 The scheme of sampling stations in the European Commission in the Kerch Strait, July 15–25, 2008 (Oil Spill… 2008)

8.5.7 Rosprirodnadzor Expeditions

The expedition investigations on the state of marine environment and bottom deposits in the Kerch Strait by the specialists from the Novorossiysk Division of the Rosprirodnadzor were conducted in three steps during July–December, 2008 (Fig. 8.14) (BSC 2010). During the first stage, from July 24 to August 31, 2008, 78 water samples and 43 samples of bottom sediments were taken; at the second stage (November), 88 and 75 samples; at the third stage (December), 64 and 36 samples, respectively. In total, 384 samples were taken and analyzed. 154 samples of bottom sediments and 230 water samples from different depths were treated. In sea water, the standard hydrochemical parameters and oil hydrocarbons (OHC) were determined. In the samples of bottom sediments, the OHC were measured.

Oil hydrocarbons in sea waters During the summer period, 2008 the OHC concentration on the Kerch Strait aquatory ranged from zero to 1.635 mg/L (33 MAC). Oil hydrocarbons which content was above the detection limit (<5 µg/L), were found in 107 samples that constituted 65% of all samples (166 horizons). The OHC concentrations exceeding the MAC during the July and August surveys were noted at 17 stations that made 10.2% of all observation depths. At other stations, the OHC concentrations during the summer expedition were within the norm. The distribution of oil products in water was characterized by patchiness, with the local zones of increased values.

In *July 24* in the surface waters two most prominent patches with OHC concentration about 33 MAC were registered inside the Taman' Bay and at one

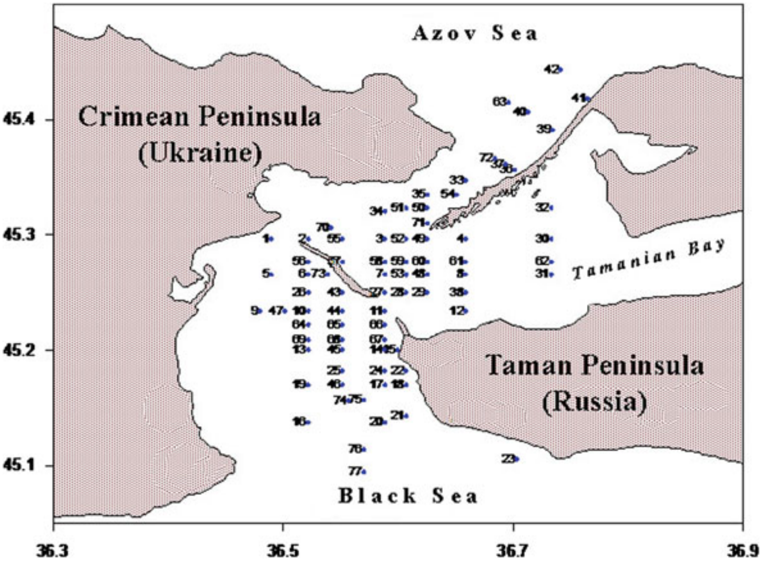


Fig. 8.14 The scheme of sampling stations in the Rosprirodnadzor expeditions in the Kerch Strait, July–December 2008

north-eastern stations near Chushka Spit (Fig. 8.15a). Also rather large content exceeded 1 MAC was noted at four stations around Tuzla Island. At all other tested points the petroleum hydrocarbons concentration was below norm 0.05 mg/l and more then half stations has it lower 0.1 MAC.

In the bottom layer the OHC distribution were almost in contrary to upper waters. The only one high patch was recorded in the southern point in the Black Sea waters with the level about 30 MAC (Fig. 8.15b). Additionally to the this local area only at three stations placed near the end of Chushka Spit and inside Taman' Bay the concentration of hydrocarbons was above 1 MAC. All other studied points showed clean waters.

In August 31 the surface concentrations of petroleum hydrocarbons were at the same magnitude as in bottom layer (Fig. 8.15c). The main part of meanings varied between analytical zero to 0.07 mg/l. Similar to upper waters southern part of area was clean and main patches of high concentration were noted in the narrowest part of the strait between ports Kerch and Caucasus, as well as on another side of the Chushka Spit. The wide coverage of northern half of the strait by waters with petroleum concentration above 0.2 MAC could be considered as a mark of large number of diffuse sources of pollution distributed over all studied area.

In November, the variability range of the OHC concentrations in the strait waters was 0.0024–0.094 mg/L, with the area-averaged value of 0.021 mg/L. The MAC was exceeded at 14 stations (9.3%). The maximum surface values of oil hydrocarbons were observed off Port Kavkaz and Cape Panagiya (Fig. 8.15d).

In the near-bottom layer three patches occurred with the space distribution similar to upper waters. The largest area of high concentration up to 1.9 MAC was distinguished offshore of Panagiya Cape (Fig. 8.15e).

In December, the concentrations of oil hydrocarbons ranged from 0.0058 to 1.1 mg/L. The mean value (0.066 mg/L) exceeded the MAC by a factor of 1.32, while the maximum value (1.1 mg/L), by a factor of 22 (Fig. 8.15f, g). The norm was exceeded in 14 samples that constituted 23% of all samples. The OHC values above 1 MAC on the surface were observed in the southern part of the strait, at exit to the Black Sea; in the near-bottom layer the increased background of oil hydrocarbons was associated with the southwestern part of the Kerch Strait.

Oil hydrocarbons in bottom sediments The spatial distribution of oil hydrocarbons in 2008 was characterized by existence of patches of high concentration (40–50 μg/g of dry weight) near the Tuzla Island and Cape Tuzla, Chushka Spit, in the Taman Bay, and at the station south of Cape Yenikale.

In summer 2008, the most polluted sites of the bottom sedimentswere (20–50 μg/g of d.w) located near the Tuzla Island, between the Chushka Spit and the Crimean coast, south of Cape Yenikale, and in the area of the westernmost tip of the Taman Peninsula, between Capes Panagia and Tuzla (Fig. 8.16a).

In winter, the centers of the maximum oil product content in bottom sediments slightly displaced that indicated the possible redistribution of polluted sediments (Fig. 8.16b). In December, the mean OHC content in bottom sediments was 56.6 μg/g of dry weight that exceeded one allowable concentration (AC) equaled 50 μg/g by criteria of Neue Niederlandische Liste (1993).

Fig. 8.15 The content of oil hydrocarbons (mg/L) in the Kerch Strait waters in 2008 (BSC 2010). *Surface layer*: **a** *July 24;* **d** *November;* **f***December. Near-bottom layer:* **b** *July 24:* **c** *August 31:* **e** *November:* **g** *December*

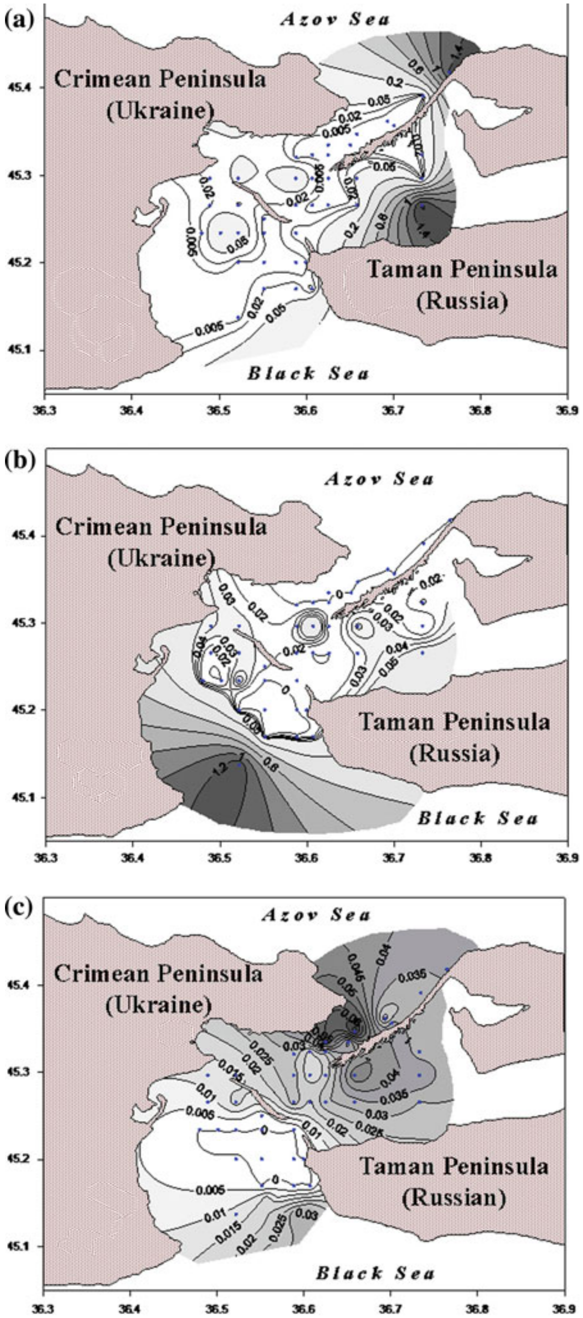
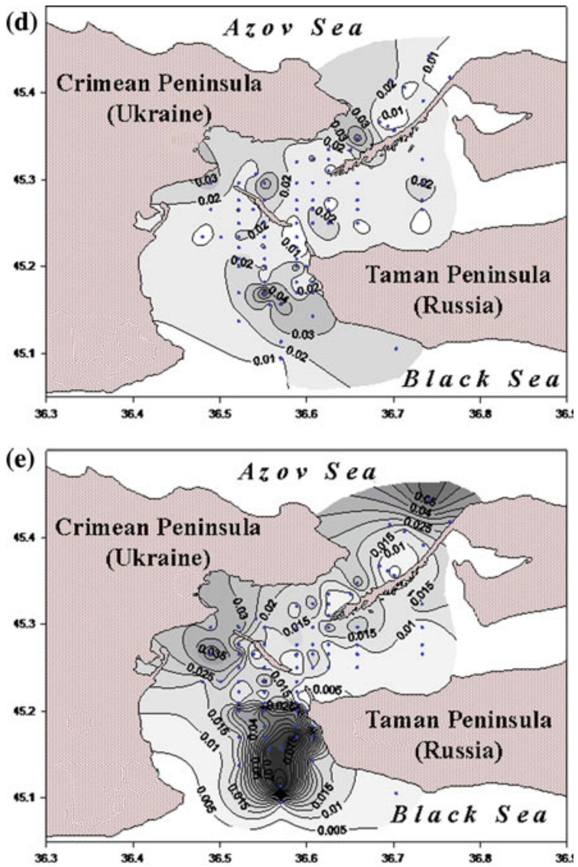


Fig. 8.15 (continued)



Now in Russia there is no the approved allowable concentrations of oil hydrocarbons for bottom sediments. According to the ground classification by degree of pollution, developed at the Black Sea Dumping Center, the sediments with the OHC content <100 µg/g belong to Class A (naturally clean ground (standard)), and those with the OHC concentration more than 100 µg/g, to Class I (conventionally clean ground). According to this classification, even the maximum value of 185 mg/kg registered in the Kerch Strait, does not allow ranging the bottom site in Class II (polluted ground, more than 200 µg/g).

8.5.8 Research Conducted by the Institute of Geography of the Russian Academy of Sciences in 2008

The Ukrainian coast of the strait in spring 2008 On March 12–14, 2008, the author (the employee of the Institute of Geography) inspected visually the areas where the

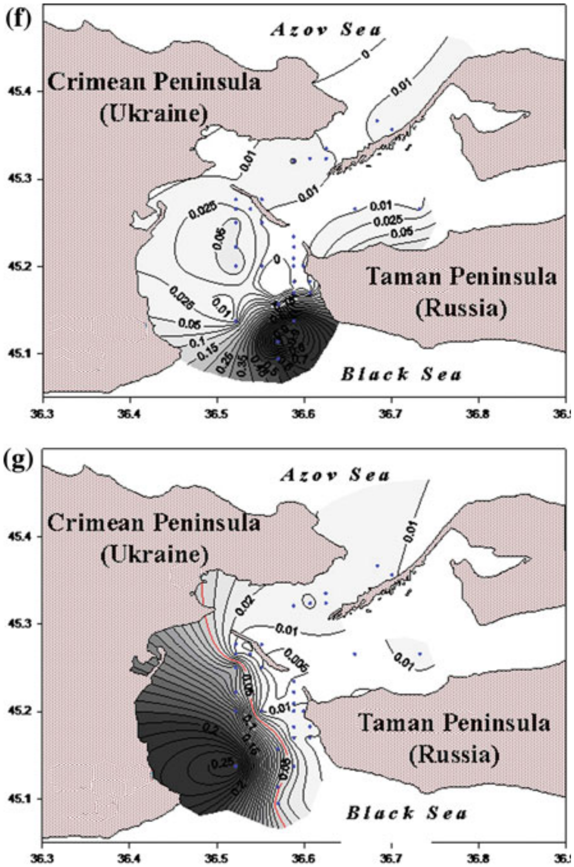


Fig. 8.15 (continued)

consequences of the tanker *Volgoneft-139* wreck were clear (Fashchuk 2009). We came round the Crimean coast of the Kerch Strait from its southern (Cape Takil, the Black Sea) to the northern (Cape Khroni, the Sea of Azov) mouth and the Tuzla Island coast. The interrogation of local residents, fishermen, employees of environmental authorities and the Ministry of Emergency Situations of Ukraine, administration of the Kerch Commercial Sea Port, participants and witnesses of the events in November, 2007 was carried out.

According to local residents, the mass appearance of fuel oil on the coast of the Kerch Bay and northern strait (settlements Kapkany, Sipyagino, Opasnoye, Port Krym, Zhukovka) during the storm on November 11 was not observed. This evidence confirmed the data of air reconnaissance of the strait on November 14, 2007, which did not found any signs of severe pollution of the Ukrainian coast of the strait in the first days after the wreck.

According to local residents, to the north of Port Krym, up to Cape Khroni in the Sea of Azov, the large-scale appearance of fuel oil on the coast was not fixed

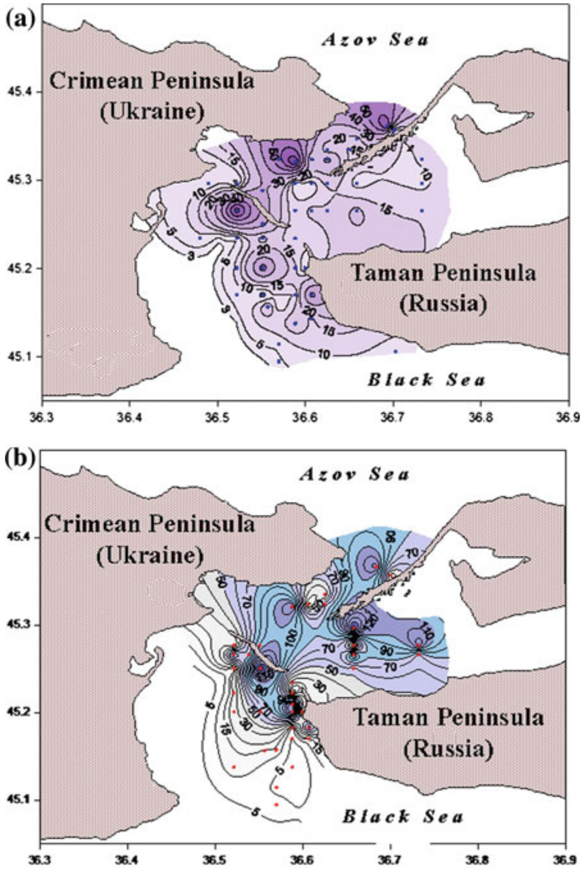


Fig. 8.16 Concentration of petroleum hydrocarbons in the Kerch Strait bottom sediment, μg/g of d.w. in August (**a**), and December (**b**) 2008 (BSC 2010)

also. At the same time, when surveying the Ukrainian coast of the Kerch strait south of Port Krym (settlement Opansoye, a beam of anchorage No. 454), the author observed the extensive coastal aquatories polluted by films of oil products and water-in-oil emulsion (Photo 8.7).

Herewith, the oil odor was felt distinctly that indicated the "freshness" of its spill. The pollution of strait waters with volatile fractions of oil products in March was not associated with the tanker wreck. Its reason was the oil losses at the continued (unauthorized) pumping of oil products on the strait aquatory.

As it was mentioned above, the wreck consequences on the Ukrainian coast of the strait, in the areas of fuel oil appearance on November 14–19, 2007, were liquidated operatively. By March 2008, the beaches of the Arshintsevo Spit and the Cape Ak-Burun bay, the territory belonging today to the Kerch historical archeological museum, turned out to be clean. Their visual survey allowed the author to find only separate stains of fuel oil in the Cape Ak-Burun bay, which remained under stones and on the rocks (Photo 8.8).

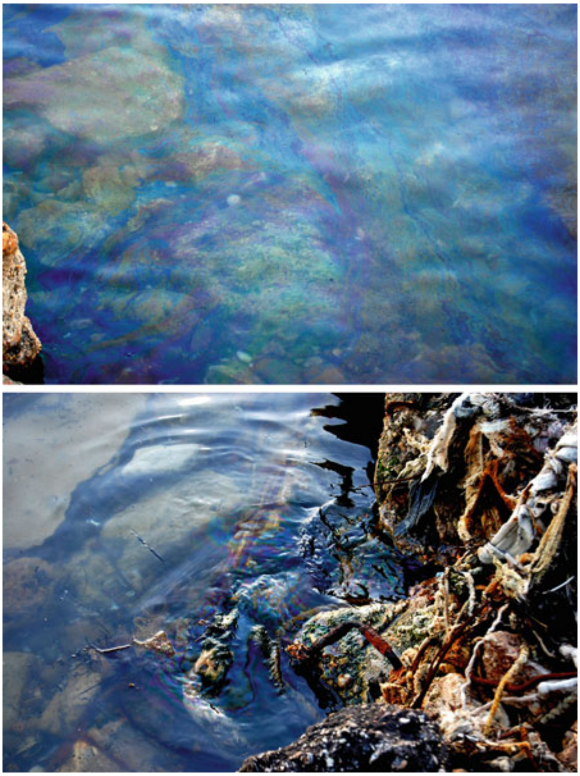


Photo 8.7 Films of recent oil products (*top*) and older oil pollution, water-in-oil emulsion, or "chocolate mousse" (*bottom*) in coastal waters of the Ukrainian coast of the Kerch Strait in the area of settlement Opasnoye (beam of anchorage No. 454 of Port Kavkaz) (Photo by the author)

Bottom of the Kerch Strait in the zone of territorial waters of Ukraine in summer, *2008*. According to the model calculations (Ovsienko et al. 2008), within four days after the wreck a considerable part of the strait aquatory and the Azov near-strait area were in the zone of fuel oil stain. After the study of the oil spill consequences in the Kerch Strait (Fashchuk 2009), it was supposed to continue the diving inspection of the strait bottom in order to improve the developed forecasts. *On August 13–25*, *2008*, for the adequate assessment of the character of the Kerch Strait bottom pollution by the residues of fuel oil spill from the tanker *Volgoneft-139* in the zone of the Ukrainian territorial waters, the Institute of Geography of the Russian Academy of Sciences conducted the visual diving survey of bottom with sampling for the analysis on the oil product content. The scheme of stations for surveying and sampling (Fig. 8.17) was developed on the basis of the results of mathematical modeling of the integral pattern of the strait pollution within six days, from November 11–15, 2007 (see Fig. 8.5), and the similar integral pattern obtained as a result of air reconnaissance of the strait on November 11–16, 2007 (Matishov et al. 2008a, b).

It was assumed that these were the zones, where the sedimentation of fuel oil to the bottom has occurred. The stations were made 1–2 km apart. In total, 41 divings with the visual survey of the bottom were made; 41 samples of sediments were

Photo 8.8 Residues of pollution with fuel oil on the rocks (*top*) and under stones (*bottom*) of Cape Ak-Burun in March, 2008 (Photo by the author)

taken. *Fuel oil was not found visually at any of 41 stations under survey*. When diving off the southern coast of the Tuzla Island (stations 31, 32, 34, and 40; Fig. 8.13) subjected to the maximum impact of fuel oil spill in the tanker wreck, the thickets of seagrass *Zostera* and considerable number of mollusk *Rapana* without the slightest signs of fuel oil were observed at the strait bottom (depths of 3–4 m). The similar picture was noted in the Tuzla channel and at the mouth of the Taman Bay (stations 24–25, Fig. 8.17).

On August 14, 2008, the Azov current (towards the Black Sea) was observed in the Kerch Strait. This day the Russian services carried out the towage of fore body of the tanker *Volgoneft 139* lifted from the Kerch Strait bottom, to Port Kavkaz. The same day, in the area of settlement Zavetnoye at the Ukrainian coast of the southern strait the specialists from the Ministry of Emergency Situations of Ukraine collected 150 bags of sea grass covered with small particles of fuel oil. The explanation of this phenomenon consists in the following.

The diving survey of the strait bottom between the Tuzla Island and Chushka Spit, along which the fore body of the tanker was towed, showed that the thickets of seagrass *Zostera* were the characteristic feature of the bottom landscape here. After dying off, the plants buoy to the surface and form floating aggregations, “islands” (Photo 8.9).

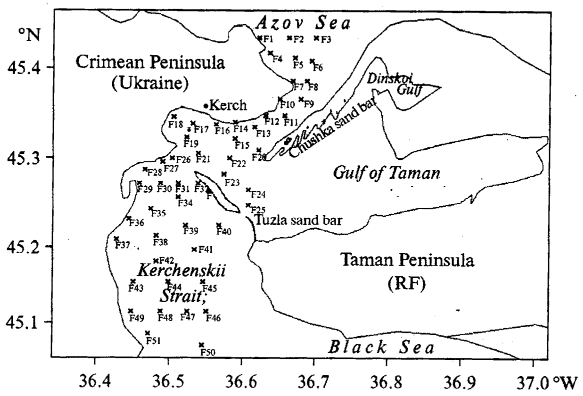


Fig. 8.17 The scheme of stations of visual diving surveying and sampling of the Kerch Strait bottom for determination of oil product content in sediments in the zone of Ukrainian territorial waters, conducted by the Institute of Geography of the Russian Academy of Sciences on August 13–25, 2008 (Fashchuk 2009)

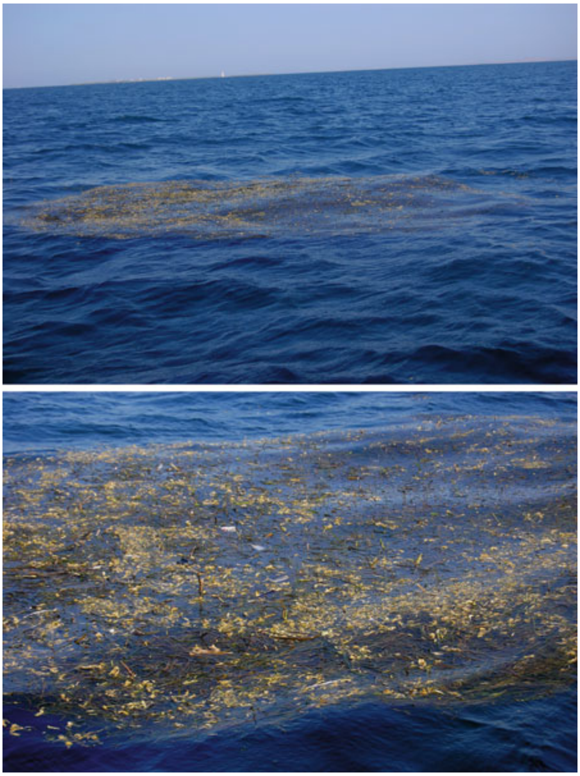


Photo 8.9 After dying off or in consequence of storm seagrass in the area of the Taman Bay mouth, between the Tuzla Island and Chushka Spit, buoys to the surface (*top*) and forms the floating "islands" (*bottom*), on which small particles of heavy fractions are accumulated in case of oil spill. *(The Chushka Spit lighthouse and Port Kavkaz terminal are seen on the horizon*; Photo by the author)

The small amount of fuel oil which got into the sea under the lifting and towage of the tanker fore body, adhered to floating grass, were transported by the Azov flow into the southern part of the strait and washed out on the beach near settlement Zavetnoye situated on the Kerch Peninsula coast, as it was predicted earlier (Photo 8.10).

Photo 8.10 The beach of the vacation hotel *Brigantina* in the southern part of the Kerch Strait, in the settlement Zavetnoye area (*top*), covered by fuel oil-polluted seagrass (*bottom*), August 15, 2008 (Photo by V. Monin)

8.6 Conclusions

The interagency field investigations conducted in the area of the tanker *Volgoneft-139* wreck in winter, 2007 and during the spring-summer season, 2008, allowed us to confirm the conclusions and prognostic estimations of the fuel oil spill fate, made on the basis of the geographic ecological analysis (Fashchuk 2007, 2008; Fashchuk et al. 2009) and model calculations of oil spill dynamics (Ovsienko et al. 2008).

During the extreme storm on November 11, 2007, under the influence of stormy southwest wind Black Sea waters penetrated into the strait zone up to Port Kavkaz. The salinity reached here 17.7‰ (Matishov et al. 2008a, b). At such salinity fuel oil of the M-100 grade transported by the tanker *Volgoneft-139* (http://www.sea.gov.ua), had neutral buoyancy and the major part of its spill was washed out by the storm on the beaches of the Tuzla Island and Chushka Spit. Fuel oil which remained in the water and was exported to the Sea of Azov, began to sink and gravitate to the bottom because at the sea salinity of 12–13‰ it was heavier than water. After the storm termination on November 14–19, the restored compensatory Azov current (see Sect. 7.4.2) "returned" the rests of the sunken fuel oil along the

Crimean coast from the Sea of Azov to the Kerch Strait, where it buoyed to the surface again (under the high salinity) and was cast ashore on the beaked sites of the Ukrainian coast, on Cape Ak-Burun and the Arshintsevo Spit. During the spring-summer season, 2008, the rests of fuel oil appeared at the strait bottom in the catastrophe epicenter zone (Tuzla and Chushka Spits, Tuzla Island), were transported by prevailing currents outside its aquatory, and by August almost the whole strait bottom, except the local sites in the heart of the Taman Bay, turned out to be cleared from the wreck consequences.

The majority of researchers, which results were presented in the monograph, came to conclusion that the consequences of the wreck on November 11, 2007 (oil pollution of water and bottom sediments in the strait) persisted only during the first months after the wreck. Following the results of the regular complex interagency observations carried out within a year after the wreck, the conclusion was drawn that *after the temporary local deterioration of environmental conditions in the Kerch Strait in the first months after the wreck (from 3000 to 14000 MACs of oil products in water and conglomerations of recent fuel oil in bottom sediments), already by May 2008, the situation concerning oil pollution of the strait waters and bottom was stabilized, and by August 2008 it was completely cleared of the accidental fuel oil spill.*

At the same time, the investigations on the content of oil products in water and bottom sediments of the Kerch Strait conducted in 2008–2009, allowed establishing the signs of the chronic environmental pollution by both the volatile (surface water) and heavy (bottom sediments) fractions of oil hydrocarbons, which exceeded considerably the consequences of the tanker *Volgoneft-139* wreck. Their constant sources could be associated with the officially forbidden (since 1990) but practically continued oil pumping from the low-tonnage barges to the large-capacity tankers at anchorage, and vice versa, and the intensive navigation and dumping of dredging grounds in the southern (Black Sea) mouth of the strait. Thereupon, the assessment of biodiversity dynamics in the Kerch Strait under the influence of natural and anthropogenic factors seems the rather urgent problem for the future geographic ecological research.

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Chapter 9
Total Conclusions

In the middle of the third century BC the Greek mathematician, philosopher, and poet Eratosthenes of Syene (circa 276–194 BC) suggested to use five latitudinal zones on the maps and was the first, who named geography as "geography". According to his calculations, the circumference of the Earth made about 25,000 miles (24,860 miles by present data). The hot zone occupied 48° of latitude on the Earth, and the 24th degree to the north and to the south of the equator was designated as a "tropic line". The cold zones occupied on 24° from the poles, being confined by the "northern and southern polar circles", and the temperate areas were located between the tropics and polar circles. For these achievements he is deservedly considered as "the father of geography" but few people know that the jealous contemporaries of Eratosthenes gave him another two contemptuous, in their opinion, nicknames, "Beta" and "Pentatlos" (Pentatlonist). By the first nickname the professional snobs indicated his minor role in many fields of science, including mathematics. The second expressed their irritation concerning a variety of his nonmathematical interests and breadth of knowledge which were over the head of the narrowly focused specialists. But in fact, by these nicknames the ancient "well-wishers" unwillingly and being unsuspicious of this, only emphasized the unique features of direction in thinking of the ingenious geographer of all ages (Ditmar 1989).

How known are such compliments to the contemporary geographers working in the field of constructive geography, from "the pontiffs of science" of different specialties, which penetrate involuntarily in the sphere of interests of these geographers and put the professional experts up to what they have already done and how this was related to the achievements in other fields of science! Today the realization of principles of marine ecological geography in practice is very often accompanied by such conflicts associated with the paradigms of professional way of thinking, difficult interagency relationships, and temper of individual researchers.

The author flatters himself that the time and experience still remain the best critics and arbiters of all ideas and hypotheses and, consequently, mutual relations among the people. No matter how high are the professional ambitions and how

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rough is the temper of allied scientists engaged in the nature research, the author is assured that sooner or later they will be convinced of the efficiency of synthesis of the results of their research within a framework of the geographic ecological approach for solving of the specific environmental problems. Perhaps, this monograph will accelerate this process. In any case, the objective reality demands it.

In the current world exploitation of marine natural resource a number of the problems and research prospects associated both with the natural (climatic) and anthropogenic (economic activities) changes in environmental conditions on our planet is obvious. In the 21st century they have been added by some legal issues, as in many regions of the World Ocean and internal seas of Russia there was an aggravation of the geopolitical situation due to discovery of new deposits and development of traditional types of marine resources, changes in the economic and political situation in some states of the CIS and corresponding relations of Russia with the leading world powers (Dobrolyubov and Fashchuk 2010).

Now the most urgent problems of the World ocean research are the following: *assessment of the World ocean impact on the global climate system state; estimation of anthropogenic changes in marine ecosystems; monitoring of marine environmental conditions in the areas of intensive economic activities; provision of marine resource users with the reliable prognostic information about the environmental conditions determining the efficiency and safety of their activity; delimitation of boundaries of the Russian economic zones in the World Ocean with Japan, Ukraine and Norway*.

Moreover, on the resolution of the United Nations, the 1998 year was declared the International Year of the Ocean. Thereupon, many countries of the world community developed the programs of research and development of their coastal waters and the wider development of the World Ocean resources [*FASI.GOV.RU/SEA*]. So, on August 10, 1998, the special resolution of the Government of the Russian Federation approved the Federal Target Program “World Ocean”. Twelve leading research institutes of Russia were involved in its development. The ultimate objective of the program is an effective use of resources and water space of the World Ocean in the interests of economic development, national safety and guarding of national sea borders. The implementation of the program is rated for 15 years, till 2012. The complex of its problems includes the international legal, commercial, industrial, transport, scientific, and strategic aspects. At the final stage of the program implementation (2007–2012), the formation of new structure of maritime activities in all specified spheres, corresponding with the needs of the future strategy of both the national development and position of Russia in the world, is suggested.

On September 2, 1999, at the National Ocean Conference held in Monterey, California, the Vice President of the United States of America Albert Gore has presented the project of the World Ocean research in the USA “*Turning to the Sea: America’s Ocean Future*”. The project stipulates the carrying out of 150 actions supported by the state in 25 scientific directions including the protection, restoration, and studying of ocean resources of the USA. The project is based on the understanding of the vital value of ocean resources in the future of the American economy, national safety, health and prosperity of the people. It is not hard to be convinced that the objectives of these two major national projects of the 21st century practically coincide.

As a result of implementation of the Russian Federal Program "World Ocean" and Al Gore's project, the huge volume of diverse interagency information will be obtained. This information will serve as a basis for solving of their main tasks. One of them is the development of new structure of scientific activity in the sphere of marine resource exploitation. The wide application of apparatus of the geographic science, including its current direction, marine ecological geography, seems a very important guarantor of the task success.

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