Geological and geochemical factors of aquatic landscapes resistance to anthropogenic influence

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Abstract. The article considers the principles of mapping, assessment of the state and degree of water bodies technogenic changes. Water bodies are represented as certain combinations of various levels lability and patterns of development geosystems – the aquatic landscape. The concept of landscape allows us to operate not with a variety of water environment factors, but with certain combinations of landscape-forming factors. Mapping and testing of aquatic landscapes make it possible to assess and normalize the anthropogenic influence not only on separate components, but also on natural complexes as a whole. Studies indicate a high degree of petroleum products and nitrogen of silts in the port zone of the Tsemesskaya Bay contamination due to the activities of the oil pumping infrastructure and ship power plants. The main factors of aquatic landscapes transformation that lead to the pollution concentration are the creation of hydraulic structures that slow down water exchange, the discharge of poorly treated drains with a high content of biogens and suspended substances, dust loss from the atmosphere. The results of geochemical studies and aquatic landscapes mapping should be used to develop indicators of environmental regulation of chemical elements in silts that are absent, which complicates the assessment of their condition and damage caused to the water body.

Keywords: Aquatic landscape, water bodies, classification, silt, suspension, chemical elements, technogenesis

1. Introduction

The analysis of the monitoring results shows that various water bodies that are equally exposed to anthropogenic flows, as a result, differ in the dynamics and degree of pollution. This is a reflection of their individuality, generated by the differences in the complex of landscape-forming factors. The most important among them are geological, geomorphological, dynamics and salinity of water masses, the nature of bottom sediments and coastal landscapes, water runoff from land, which determine the physical and chemical parameters of the environment, the intensity of intake and the system of compounds that affect the migration activity of chemical elements in a water body. As a result of their interaction, naturally changing and relatively homogeneous natural complexes of aquatic geochemical landscapes are formed in water bodies [1], every of which differs in its own set of external migration factors, the
concentration and ratio of chemical elements in water, silts, suspensions and living organisms, react differently to external influences [2].

2. Classification and geoeological mapping of aquatic landscapes

Aquatic landscapes, as a rule, are located in the depressions of the Earth's crust, and are an accumulative element of cascading landscape-geochemical systems. Therefore, colossal masses of natural and anthropogenic chemical compounds that were previously in an immobilized state or were previously absent at all, involved as a result of nature use in an active biogeochemical cycle, are eventually carried out (including by air) into water bodies. Their future fate is determined by the parameters of the environment in which they arrive. Depending on its landscape-geochemical conditions, substances are dispersed or localized. The result of localization is often pollution of the environment and especially its most conservative component-silt. All this puts the methodology of landscape geochemistry into the basic ones for biosphere research and leads to the need to systematize landscapes for mapping and natural-functional zoning of water bodies, which is based on factors that determine the migration of chemical elements.

The classification of aquatic landscapes uses the same taxonomic parameters (characteristics of technogenic, biogenic, physico-chemical and mechanical migration) as in land, but in a modified form (table 1).

Table 1. Classification of aquatic geochemical landscapes [2]

| Types of migration | Factors of geochemical migration | Structural units of the landscape |
|--------------------|---------------------------------|----------------------------------|
| Biogenic           | Primary production of organic matter | Low-productive | Medium-sized production | Highly productive |
| Physico-chemical   | Type of redox zonning            | Oxygen | Oxygen-gel | Oxygen-hydrogen sulfide weakly restored | Hydrogensulfide |
|                    | Alkaline-acid conditions         | Sour   | Slightly acidic | Neutral | Slightly alkaline |
|                    | Mineralization and hydrochemical class of waters | Fresh | Slightly salty | Salty | Strongly salty |
| Mechanical         | Geomorphology and hydrodynamic regime | Abrasive | Transaquatic | Transaccumulative | Accumulative |
| Type of bottom sediments | Granulometric composition | Sand | Large silstone fine-aleuriticsilt | Lime | Clay silt |
|                    | Carbonate content               | Terrigenous | Slightly lime | Highly lime | |

The topology of all aquatic landscapes uses the same taxonomic parameters. Individual sections of the World Ocean are distinguished by a peculiar geochemical coupling of landscapes: estuaries and bays, estuaries, coastal zone, shelf, continental slope and central basin. The main difference between aquatic landscapes and land landscapes is a closer relationship (turning into interdependence) between different components or coherence [3]. A closer relationship between the factors determining the
migration of chemical elements leads to the fact that five main groups of aquatic landscapes are distinguished [1], which are transformed in different conditions of the World Ocean.

For example, A. D. Khovansky proposed to distinguish at least 15 geochemical landscapes during small-scale mapping of the Black Sea [4]. Within the Russian sector of the Caspian Sea, K. M. Petrov (1999) proposed to allocate up to 9 natural-territorial complexes based on the approach to zoning of aquatic landscapes developed in [1] The typification is based on such characteristics as relief, bottom sediments structure, types of bottom communities. A similar approach developed for the zoning of the water landscapes of the Azov Sea using elements of GIS technologies (Bespalov, Berdnikov, 2005) also shows the possibility of taking into account both abiotic and biotic indicators during zoning. Such an approach to geoeconomic zoning of territories should precede the allocation of environmental sensitivity zones, sustainability, pollution, otherwise the objectivity of the assessment will be low. Since the reaction of biogeocenoses to anthropogenic influences can vary significantly in different areas and conditions. This is the result of the fact that the aquatic landscapes of the water body have different assimilation potential.

3. Assimilation potential and sustainability of aquatic landscapes

Assimilation potential is the ability of the natural environment to process and neutralize harmful substances (production waste) without deterioration of the basic properties. In this sense, the assimilation potential can be considered as a natural resource that has its own economic assessment reflecting its value. Its presence allows to partially dump production waste into the environment and save on their purification [5].

The ecosystem assimilation capacity is defined as an indicator of the maximum dynamic capacity of the toxicants amount or impacts that can be accumulated, destroyed, transformed and removed from the ecosystem without disrupting its normal activity per unit of time. The capacity of the assimilation potential is determined by the ability of ecosystems to self-purification, removal and dilution of pollutants, biological diversity, dynamism of processes, the possibility of intra-system metabolism, the ability to temporarily transform or release chemical compounds to reduce the effect of external influence (negative feedback) [5].

The assimilation capacity value depends on a variety of natural and technogenic factors, as well as the pollution physico-chemical properties. However, biological processes are decisive. For example, when assessing the assimilation capacity of water bodies, three main processes can be distinguished: hydrodynamics, microbiological decomposition of pollutants and biosedimentation (biological deposition). A similar approach is taken by A. D. Khovansky, according to which the stability of water landscapes depends on the intensity of the scattering processes, dilution and decomposition of matter occurring in them [1].

On land, a wider range of natural and anthropogenic features is involved in the formation of the assimilation potential of landscapes. In general, the factors that determine the stability of landscapes, according to M. A. Glazovskaya and N. P. Solntseva, can be combined into the same three groups [6,7]:

- determining the intensity of removal and scattering of technogenesis products;
- determining the intensity of transformation of technogenesis products;
- establishing the initial capacity, the possible intensity and strength of fixing the products of technogenesis and their metabolites in natural systems.

It should be noted that the resistance of landscapes to the same pollution agents or types of anthropogenic influence is not the same. In addition, the stability of the same landscape or the natural system elementis a variable value. It may depend on the time of year, the general condition or the phase of the system development. The factors that ensure the stability of ecosystems to various types of technogenesis are also different. All this led to the substantiation of M. A. Glazovskaya's concept of ecological and geochemical stability and the identification of special landscape-geochemical systems-technobiogems, which combine into landscapes that are similar in terms of stability and the nature of the reaction to the same type of technogenic influences [6]. In the development of this approach, N. P. Solntseva justified the principle of geochemical compatibility due to qualitative criteria for the stability
of natural systems in relation to various types of anthropogenic influences [7]. The criteria and integral characteristic of ecological and geochemical stability were defined by M. A. Glazovskaya (at the suggestion of N. S. Kasimov, they are called the Glazovskaya pollution rule): "The indicator of the landsca

cenosis normal functioning is its biological productivity and the quality of biological products created: the level of productivity should not decrease, elements in quantities that violate the vital functions of organisms should not accumulate in the biomass, a useful gene pool should be preserved in the soil biota" [3].

4. Technogenic transformation of the Tsemesskaya Bay aquatic landscapes

Let's consider the results of technogenic transformation of aquatic landscapes on the example of Tsemesskaya Bay. The Novorossiysk port is located here, the largest transport hub in Russia, with a capacity of more than 6 thousand ships and 400 million tons of cargo per year. The most important components of cargo turnover are oil and petroleum products (80%), ferrous and non-ferrous metals, chemical compounds, etc. Dredging, soil movement, the creation of new jetties and berths, are taking on an increasing scale, being part of the port reconstruction general scheme. This leads to a slowdown in water exchange and an increase in pollution of coastal waters, which negatively affects biocenoses.

The violation of the hydrochemical regime due to domestic and industrial effluents, the polluted Tsemess River draining the entire valley, anthropogenic desalination of coastal waters, leaks of petroleum products, etc., has a great impact on the sea inhabitants.

The most resistant to the main factor of water area pollution – oil products are brown algae (cystose). Less stable are green (ulva) and red (ceramium) algae. A decrease in resistance to the action of oil and diesel fuel has been experimentally shown in the series: brown (cystose) → green (ulva) → red (ceramium) algae [8]. One of the significant indicators of the increase in the biogenic and organic substances concentration in coastal waters is the change in the number of algae accompanying cystosire. One of the anthropogenic influence consequences is an increase in water turbidity. The euphotic zone in the Black Sea has been noticeably decreasing in recent decades. When comparing the results of different decades, it was revealed that the biomass of cystosyra at the optimal depths for its growth practically did not change. However, the width of its thickets has significantly decreased as a result of raising the lower border of the phytocenosis from 15-20 to 10 m [8].

According to the composition of bottom sediments, as a result of the all landscape-forming factors interaction, seven main biotopes can be distinguished in the Tsemesskaya Bay [9]:

1) black aleurite -pelitic silt, which is located in the top of the bay, fenced off by moles, at the confluence of the Tsemess River. The bottom sediment is characterized by the maximum values of natural humidity (up to 71.5 %) and chloroform bitumen (1.32 g/100 g of sediment), has a liquid consistency, the smell of oil and in places hydrogen sulfide, which indicates the environment reducing conditions;

2) further from the Tsemess River mouth (behind the seaport), dark coastal silty sand dominates, located at a depth of 5-10 m, which is characterized by a chloroform bitumen high content (0.11-0.14 g/100 g of sediment), which is not typical for sandy soils (natural humidity up to 34.9 %) and is the result of pollution;

3) aleurite silt is widespread in the middle part of the bay, which occupies the most extensive area at depths of 20-24 m. The bottom sediments here are with a brown oxidized surface layer. These soils have a lower natural humidity – up to 40.7 %, contain less chloroform bitumen (up to 0.16 g/100 g of sediment), organic carbon and total nitrogen. At the eastern shore, near the outlet of the wastewater treatment facilities of the oil terminal "Sheskharis", aleurite silt turns into pelitic silt, similar in its physico-chemical properties to the port bottom sediments. It is black in colour with a metallic luster and a higher content of chloroform bitumen and natural moisture;

4) large sand with shell, located between the rocky outcrops on the bottom, with the muddy zone of the bay middle part in two strips along the shores at a depth of 10-20 m;

5) clean coastal sand at the exit of the bay;

6) clean muddy sand at great depths in the central part at the exit of the bay;
7) deep-sea aleurite silt at depths of more than 40 m at the exit of the bay. Thus, as moving from the port to the exit from the bay, the amount of chloroform bitumen in the bottom sediments gradually decreases to hundredths of a gram, organic carbon-to tenths of a percent and nitrogen-to hundredths of a percent, the granulometric composition of the soils becomes lighter, and hydrogen sulfide disappears in the silts. The purest bottom sediments related to sands are observed in the Kabardinka area.

If it operates with the generalizing concept of an aquatic landscape, then according to the degree of increase in the technogenic load, the aquatic landscapes form the following series: low-productive oxygen transaqual on the sands (at the exit from the bay) → medium-productive oxygen-gley transaccumulative on siltstones → medium (high)- productive oxygen-hydrogen sulfide transaccumulative on aleuropelite silts → highly productive (low-productive) hydrogen sulfide accumulative on clay silts. Such a natural transformation of aquatic landscapes makes it possible to actively use the methods of landscape-geochemical mapping when monitoring and assessing the state of the water area and indicates an increase in recovery processes and their movement from silt into the water column, as well as a change in the granulometric composition of sediments. It should be noted that the last types of aquatic landscapes are found in the coastal part in spots, almost at every exit of the storm drain or the place of the streams confluence.

The greatest destruction of phytocommunities, as a visible result of the manifestation of technogenic impact, is observed in the port waters. One of the leading factors is chemical pollution. Toxic substances from the air and water pass into the ground. Therefore, the study of the toxicological state of the aquatic environment and bottom sediments is of great importance for the entire biota and for understanding the fish stock formation processes.

Constant, significant concentrations of hydrogen sulfide, thiosulfate and sulfur in the bay water were not registered [8]. That is, there are no zones of hydrogen sulfide contamination covering the entire water column. After the restoration of water aeration, hydrogen sulfide and other reduced forms of sulfur disappear quite quickly. But hydrogen sulfide is found almost everywhere in the bottom sediments of the port. Here only the thin upper layer of the bottom soil has a brown colour, which is typical for oxidized forms of metals, and deeper than 1-3 cm there are layers of black colour with a characteristic hydrogen sulfide smell. This indicates a relatively good aeration of the water column in the port water area up to the lower horizons.

As for heavy metals, in the port water the water area periodically (mainly in summer) there is a 2-3-fold excess of the MPC (maximum permissible concentration) for iron; a 5-fold excess of the MPC for Mn, Cu, Pb. According to Zn and Cd, moderate levels of pollution were detected at most stations. The maximum exceedances of the MPC-up to 6-12 times, are noted at some stations according to Hg. The concentration of sulfides of these heavy metals at the background point (in the center of the bay) is three times lower than the average value in June and September and zero in July [8]. A similar geochemical specificity of pollution was found earlier in the waters and silts of the northwestern part of the Black Sea [1] and is consistent with our data on the pollution of urban dust in Novorossiysk. Spectral analysis showed that it is enriched with the same chemical elements (table 2) that water suspensions and the coastal part silts.

Table 2. Average (n*10^{-3} mas. %, with a probability of 95 %) the content of trace elements in urban dust

| Indicators | Cu   | Zn   | As   | Ag   | Bi   | Pb   | Cr   | Sn   | Mo   | W   | Co   |
|------------|------|------|------|------|------|------|------|------|------|-----|------|
| Average    | 13.8 | 38.0 | 2.11 | 0.0974 | 0.26 | 10.3 | 9.6  | 0.58 | 0.31 | 0.17 | 1.50 |
| Mistake    | ±5.8 | ±13.9 | ±0.32 | ±0.07 | ±0.21 | ±6.2 | ±2.7 | ±0.11 | ±0.09 | ±0.07 | ±0.17 |
| Indicators | Ta   | Ga   | Ge   | P    | Li   | Sr   | V    | Ba   | Ti   | Ni  | Mn  |
| Average    | 0.10 | 1.39 | 0.12 | 40.3 | 3.16 | 38.4 | 9.1  | 133  | 384  | 3.58 | 81.6 |
| Mistake    | ±0.02 | ±0.21 | ±0.03 | ±14.6 | ±0.37 | ±6.9 | ±2.5 | ±110 | ±166 | ±0.69 | ±14.2 |
Relatively to the regional clark a microelements in technogenic aerosols form the following series for reducing the enrichment degree: Ag (6.99) > Zn (5.19) > Pb (4.48) > Cu (2.6) > Sr (1.88) > Va (1.78) > Sn (1.09) > Mo (0.99) > Mn (0.94) > Cr (0.86) > Co (0.78) > Ga, Ni (0.73) > Ti (0.70) > V (0.67). Thus, urban aerosols are sharply enriched with Ag, Zn, Pb and Cu elements with polymetals that are completely uncharacteristic of local, mainly carbonate (mainly marl) rocks. In this regard, it would be more justified to enrich the dust with Sr and Va. All this is the result of the increased technophilicity of these chemical elements [10] and their concentration in sulfides after dust enters the water area, with low oxidability of bottom waters and silts.

The petroleum products distribution in the bottom sediments is also uneven and is observed in the concentration range of 0.13-1.61 mg/kg, i.e. by more than an order of magnitude. The average concentrations for each observation period are close to each other (0.88-0.98 mg / kg), reflecting a stable level of contamination. As in the distribution of sulfides, the minimum concentrations of petroleum products are confined to the bay central part. The accumulation of phenols in bottom sediments is more homogeneous and varies over the entire observation period from 0.5 to 2.7 micrograms/g. Unlike petroleum products and sulfides, the highest level of pollution with phenols is manifested at stations affected by fresh water flow [8]. An analysis of our data on the Tsemesskaya Bay (port water area) and a comparison with the stock materials of the “Federal research centre the southern scientific centre of the Russian academy of sciences” over the past ten years indicates a relatively high contamination of bottom sediments (at individual stations) with petroleum products and trace elements.

The deterioration of the ecological situation is also noted in the water of the much less technogenically loaded the Anapa beach area. And here the negative consequences are the result of a combination of two factors – a decrease in the assimilation potential of the aquatic landscapes and an increase in the anthropogenic load. The degree of technogenic influence on water exchange here is much less, due to the greater bay openness, but this does not save from the deterioration of water quality and bottom sediments in the zone of the most bay anthropogenic-laden beaches. Therefore, the sanitary and hygienic characteristics of the open sea beaches and in the bay in the summer period differ radically, which requires active intervention by reclamation of bottom sediments and beach soils [11].

5. Conclusion
1. In general, the geochemical specificity of the bay silt pollution is consistent with other regions [12, 13] and the features of the Novorossiysk urban dust noted by us. Everywhere, the main factors of pollution are such heavy metals as Zn, Cu, Pb, and a high level of contamination of silts by them is accompanied by a weighting of the granulometric composition of bottom sediments due to the deposition of suspended particles.
2. It is impossible not to note the high degree of the port zone silts contamination with petroleum products and nitrogen due to the activities of the oil pumping infrastructure and ship power plants [14].
3. The main factors of aquatic landscapes transformation that lead to the concentration of pollution are the creation of hydraulic structures that slow down water exchange and discharge of poorly treated wastewater with a high content of biogens and suspended substances (especially in the shallow water zone).
4. The results of geochemical studies and mapping of aquatic landscapes should be used to develop indicators of environmental regulation of chemical elements in silts (similar to soils [15]), which are absent, which complicates the state of silts assessment and the damage caused to water bodies.
5. When determining the directions of coastal part and water areas of water bodies transformation, mapping and assessment of the water landscapes state should be carried out, for subsequent natural and functional zoning of water bodies from a variety of positions, including from the point of view of their stability. This will allow to simulate the response to the technogenic influence, to assess the buffer capacities and assimilation potential of various sections of reservoirs, which are largely determined by their landscape-geochemical features.

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