Landscape-geochemical principles for assessing the state of water bodies and their resources

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Abstract. The principles of assessing the state and degree of technogenic transformation of water bodies are considered. Water bodies are presented as certain combinations of geosystems of different levels of lability and developmental patterns - aquatic landscapes. The concept of an aquatic landscape includes not only the water column itself, but also bottom sediments, suspended matter, and various living matter. The use of the concept of landscape makes it possible to operate not with a multitude of factors of the aquatic environment, but with certain combinations of landscape-forming factors. Classification, mapping and testing of aquatic landscapes make it possible to monitor, assess and standardize the technogenic impact not only on individual components, but also on natural complexes in general. The research results show that the differentiation of natural conditions causes significant fluctuations in the natural background of silts of various aquatic landscapes. Therefore, in order to develop normalized characteristics of the background and anomalous distribution of chemical elements, it is necessary to test and analytically study silts of the main landscapes. Under the influence of technogenesis, not only pollution occurs, but a natural transformation of aquatic landscapes in the direction of intensification of recovery processes and their movement from silts into the water column, accompanied by a change in the granulometric composition of the silts.

1. Introduction
Assessment of the state of water bodies and identification of pollution is a difficult task due to the complexity of their structure, the combination of geosystems with different levels of lability and developmental patterns. The concept of aquatic landscapes includes not only the water column itself (upper and bottom layers separately), but also bottom sediments, suspended matter, and various living matter. Here we have both a very dynamic migration environment - water, and a depositing component - silts. In water, pollution spreads and dilutes quickly enough, which is determined by the hydrological characteristics of the water body. In silts, pollution accumulates during the entire period of their existence and depends not only on the hydrodynamic characteristics, but also on the lithological and geochemical characteristics of bottom sediments. Naturally, they require different approaches to mapping and assessing their condition.
2. General characteristics of the research object

In general terms, an aquatic landscape is a body of water with the same plant communities, the same type of geochemical environment in water and silts, located on homogeneous relief elements, within which a certain type of bottom sediments is formed. The use of the concept of landscape makes it possible to operate not with a multitude of factors of the aquatic environment, but with certain combinations of landscape-forming factors. As a result, it becomes possible to assess and standardize the technogenic impact not only on individual components, but also on natural complexes as a whole.

The state of aquatic landscapes depends on the proximity to the source of pollution, the intensity of self-purification and sedimentation processes, as well as the dynamics of the water mass. It is known that under the influence of technogenesis and progressive pollution, they go through certain stages of transformation of the biological component and physicochemical characteristics [1]. Thus, mapping of aquatic landscapes makes it possible to assess the state of the water body, and sampling of silts – to assess the composition and intensity of accumulated pollution.

The main problem is that the maximum permissible concentrations (MPC) are the indicators of the ecological state of surface waters separately for drinking and fishery water bodies. For silts, there are no such criteria, which generates uncertainty in assessing the state and impact of technogenic factors on water bodies. This problem can be solved by a landscape-geochemical approach to assessing the state of the components of the biosphere, which is a universal approach, especially when normalized characteristics are absent or raise reasonable doubts about their objectivity. This often applies to soils, plants and other biological objects. Since the methodology of landscape geochemistry is based on the relationship between climate, rocks, relief, soils, vegetation, waters and the content of chemical elements and compounds, landscapes can be distinguished by physical-geographical and geological data without the use of special geochemical materials, which simplifies their differentiation and mapping [2].

3. Classification and mapping of aquatic landscapes

In the classification of aquatic landscapes, the same taxonomic parameters (characteristics of technogenic, biogenic, physicochemical and mechanical migration) are used as in terrestrial ones, but in a slightly modified form [1,2].

At the first stage, aquatic landscapes are divided into technogenic (reservoirs, canals, sedimentation tanks) and natural ones. Further, when identifying both natural and technogenic elementary aquatic landscapes, the following components are taken into account in turn: species composition, biomass and production of plant communities; oxidation-reduction conditions, alkaline-acid conditions, typomorphic components in water, bottom layers and bottom sediments; geomorphological structure and hydrodynamic regime; type of bottom sediments.

All aquatic landscapes are classified on the basis of the same taxonomic parameters. The approaches to the analysis of the geomorphological structure and hydrodynamic regime of rivers, reservoirs and seas differ most noticeably. Some areas of the world ocean are distinguished by a peculiar geochemical conjugation of landscapes: estuaries and bays, coastal zone, shelf, continental slope and central basin.

The main difference between aquatic and terrestrial landscapes is an even closer relationship (turning into interdependence) between various components or coherence [3]. Therefore, water bodies consist of regularly changing relatively homogeneous complexes - geochemical landscapes, each of which is distinguished by individual characteristics of formation, certain relationships and patterns of geochemical migration. A closer relationship between the factors that determine the migration of chemical elements leads to the fact that there are five main groups of aquatic landscapes [1]:

1) oxygenic transaquatic (trans-erosive, abrasion) landscapes on sands or shell rocks, located in areas with intensive water dynamics;

2) oxygenic-gley (oxygen conditions in water and gley in silts) trans-accumulative landscapes on aleuritic silts are formed under conditions of decreased hydrodynamic activity and sedimentation of suspended matter (shallows in rivers, leveled shelf areas);
3) oxygenic-hydrosulfuric accumulative landscapes on aleuropelitic and clayey silts are formed in low or quiet areas, where fine suspended matter and organic matter accumulate, and the oxygen content in the bottom waters can decrease to zero;

4) hydrosulfuric accumulative landscapes on clayey silts are reformed in the deep sea zone (Black Sea). Oxidizing conditions persist only in the upper water layers;

5) oxygenic-gley accumulative landscapes on glauconite-foraminiferal aleurites are formed under the specific conditions of the upper part of the continental slope.

Under the influence of technogenesis, a regular transformation of aquatic landscapes occurs in the direction of intensification of recovery processes and their movement from silts into the water column, as well as a change in the granulometric composition of silts: low-productive oxygenic transaquatic on sands → medium-productive oxygenic-gley trans-accumulative on silts → medium (high)-productive oxygenic-hydrosulfuric trans-accumulative on aleuropelitic silts → highly productive (low-productive) hydrosulfuric accumulative on clayey silts. Such a natural transformation of aquatic landscapes makes it possible to actively use the methods of landscape-geochemical mapping in monitoring and assessing the state of water bodies and watercourses.

Lithological, geochemical, bathymetric, hydrochemical and hydrobiological maps are basis for making maps of aquatic geochemical landscapes. The use of these materials makes it possible to compile separate auxiliary maps for each type of migration: 1) plant communities, biomass and phytoplankton production; 2) types of geochemical environment; 3) conditions of mechanical migration; 4) types of bottom sediments. Their sequential combination (translation of the contours from all four tracing papers to one) and adaptation make it possible to identify areas with the same combination of migration factors, that is, geochemical landscapes.

The landscapes identified in this way are characterized by a different set of external migration factors that determine their functioning and geochemical features. The landscape approach to geoecological mapping and assessment of the state of the environment is especially important in the study of silts, soils and plants, since "it allows us to establish the most probable content of chemical elements in them even in untested fragments of the region, based on the results of mapping and studying similar (landscapes)" [2]. This is very important with the existing methods for assessing the state of the environment, which ignore the landscape and regional diversity of the biosphere and rely on the concept of sanitary and hygienic regulation using uniform standards for the whole country.

Identification of these relatively homogeneous complexes makes it possible to operate not with a multitude of factors of the aquatic environment, but with certain combinations of them - structural units of water systems characterized by certain natural conditions and interrelationships between components [1]. This provides a transfer to a new level of research and allows us to move on to assessing and regulating the technogenic impact on natural complexes as a whole, and not on individual components: silts, water, algae, etc.

4. Geochemical characteristics of silts

Bottom sediments are the most stable and representative component of the aquatic ecosystem. Different aquatic landscapes (as well as terrestrial ones) are characterized by unequal self-purification potential and the degree of fixation of polluting components. This is especially important due to the lack of environmental standards for silts. It is possible to assess the degree of their pollution only by establishing the background characteristics of the distribution of pollutants in unpolluted aquatic landscapes by testing, analytical work and statistical processing of their results [1].

Most of the substances entering water bodies eventually settle on the bottom. Therefore, the composition and properties of silts reflect the entire set of biological, physical, chemical and man-made processes undergoing in the water area and the impacts made earlier. And, in comparison with the labile aquatic environment, they are a more conservative component of aquatic landscapes, fixing and accumulating pollutants. As a result of intense pollution, silts can become a secondary source of pollution, the so-called "ecological time bomb". The study of silts and the identification of
geochemical anomalies in them makes it possible to more fully appreciate the nature and extent of pollution of water bodies.

Often, this can be a consequence of long-range atmospheric transport of man-made emissions. Our studies of aerial mechanisms of water resources pollution allowed us to establish that the pollution found in silts and water suspension of the Black Sea can be caused by the fallout of dust that forms in settlements, industrial and road landscapes. 50 dust samples were taken in different parts of Novorossiysk, at different distances from sources of technogenic aerosols and at different heights. Spectral analysis showed that it is enriched with the same chemical elements (Table 1) as water suspensions and silts of the coastal part.

**Table 1.** Average (n*10⁻³ mass percent, 95% probability) content of trace elements in city dust

| Indicators | Cu | Zn | Pb | Ag  | Bi | As | Cr | Sn | Mo | W  | Co |
|------------|----|----|----|-----|----|----|----|----|----|----|----|
| Average    | 13.8 | 38.0 | 10.3 | 0.0974 | 0.26 | 2.11 | 9.6 | 0.58 | 0.31 | 0.17 | 1.50 |
| Error      | 5.8 | 13.9 | 6.2 | 0.07 | 0.21 | 0.32 | 2.7 | 0.11 | 0.09 | 0.07 | 0.17 |

| Indicators | Ta | Ga | Ge | P  | Li | Ti | V  | Ba | Sr | Ni | Mn |
|------------|----|----|----|----|----|----|----|----|----|----|----|
| Average    | 0.10 | 1.39 | 0.12 | 40.3 | 3.16 | 384 | 9.1 | 133 | 38.4 | 3.58 | 81.6 |
| Error      | 0.02 | 0.21 | 0.03 | 14.6 | 0.37 | 166 | 2.5 | 110 | 6.9 | 0.69 | 14.2 |

With respect to the regional clarke, the trace elements in technogenic aerosols form the following series in terms of the decrease in the degree of enrichment: Ag (6.99)>Zn (5.19)>Pb (4.48)>Cu (2.6)>Sr (1.88)>Ba (1.78)>Sn (1.09)>Mo (0.99)>Mn (0.94)>Cr (0.86)>Co (0.78)>Ga, Ni (0.73)>Ti (0.7)>V (0.67). Thus, urban aerosols are sharply enriched in Ag, Zn, Pb and Cu - polymetal elements that are completely uncharacteristic of local, predominantly carbonate (mainly marl) rocks. In this regard, it would be more reasonable to expect enrichment of the dust with Sr and Ba.

As a result of the fallout of pollution from the atmosphere, the drift of substances from the land, the differentiation of natural conditions, significant fluctuations in the natural background of silts of various aquatic landscapes arise, as in the case of soils [4]. Moreover, along with the background ones, the anomalous values required for the detection and assessment of pollution also differ significantly. For example, in the northwestern part of the Black Sea, the sharpest differences in average concentrations - 3-10 times typical for Ni, Cu, V, Pb and other microelements. As a result, the background contents of Ni and V in fine aleuritic silts of oxygenic-hydrosulfuric landscapes are anomalous even for single samples in the sands of oxygenic landscapes [5]. The latest studies of the water resources of the Sea of Azov in the area of the port of Temryuk recorded fluctuations in the background content of heavy metals by almost an order of magnitude [6]. And there are many such examples in a wide variety of water bodies.

Thus, the background contents of chemical elements in some landscapes may be anomalous for others. As a result, when assessing the state of water bodies and identifying contaminated areas without taking into account the natural geochemical differentiation of aquatic landscapes, it is possible to obtain clearly false anomalies associated not with pollution, but with the natural change of landscapes or geochemical barriers (barrier zones), on which a variety of chemical elements are concentrated even under conditions of background parameters of the migration flow and which can be removed from the pollution source at a distance of tens of kilometers. When developing ecosystemic regional and local indicators for soils, silts, surface waters in order to assess their condition and damage caused, to conduct monitoring and cadastre, it is necessary to use the parameters determined on the basis of the results of landscape-geochemical mapping and testing of specific territories, as provided by law [7].

5. Geochemical barriers and barrier zones in aquatic landscapes

The above data indicate that each landscape is distinguished by a complex of landscape-forming factors, the concentration and combination of chemical elements in all ecosystems. This means that it
has an individual geochemical field with certain characteristics. The proximity of landscapes with sharply different geochemical fields leads to the formation of various parameters of mass transfer of matter at their border, as well as a gradient of concentrations of chemical elements. As a result of such a sharp change in the conditions of migration of chemical elements in conjugated landscapes or in their subsystems, the boundaries between them turn into geochemical barriers.

The geochemical barrier is the term for the areas of the earth's crust, in which, at a short distance, there is a sharp decrease in the intensity of migration of chemical elements and, as a result, their concentration increases. As a result of changes in the landscape-geochemical environment and the conditions of migration of elements, many of them pass from a mobile state to a stationary one and accumulate at the border between different environments. Depending on the direction of migration, radial and lateral barriers are distinguished. The former emerge during vertical migration, the latter - during subhorizontal migration.

The theory of geochemical barriers was developed by A.I. Perelman [3,8]. In accordance with the main types of migration, he identified three types of geochemical barriers: mechanical, physicochemical (oxidative, hydrosulfuric, gley, alkaline, acidic, evaporative, sorption, thermodynamic, sulfate barriers) and biogeochemical ones. In real conditions, all types of migration are closely interrelated, therefore, complex barriers are often distinguished, which are formed as a result of the superposition of several geochemical processes. According to the conditions of formation, geochemical barriers are divided into natural and technogenic ones and, according to the scale of manifestation, into macro-, meso- and microbarriers.

The activity of geochemical barriers is responsible for the formation of natural and man-made geochemical anomalies, as well as mineral deposits. The higher the contrast of the environments of neighboring landscapes or their subsystems and the more intense the migration flow, the greater the capacity of the geochemical barrier, the wider the barrier zone and the higher the concentration of chemical elements. The increase in the scale of anthropogenic activity contributes to the formation of technogenic geochemical anomalies, which are pollution zones, and puts forward the theory of geochemical barriers among the most important in solving environmental problems.

Thus, the concepts of geochemical setting, geochemical barriers and geochemical fields are closely interrelated and are a function of a wide range of landscape-forming factors and the radial structure of landscapes. Landscapes that differ in at least one taxonomic parameter or characteristics of subsystems naturally differ in the concentrations and ratios of chemical elements in water, silts and plants, in the presence and intensity of geochemical barriers activity, as well as in response to anthropogenic impact. This response and the buffering capacity of landscapes largely determine their resilience and assimilation potential. Therefore, in solving the problems of determining and taking into account the specifics of the assimilation potential of water areas, an important role belongs to geochemistry and mapping of aquatic landscapes. Methods for identifying and systematizing landscapes make it possible to carry out natural-functional zoning of water bodies from a variety of positions, including from the point of view of the sustainability of their assimilation potential.

6. Landscape-geochemical studies of water resources and assessment of the state of the environment

The final materials of the landscape-geochemical study are an ecological-geochemical database, maps of geochemical landscapes and tables containing parameters of the background and anomalous distribution of chemical elements in silts (algae, water) of various landscapes, as well as maps of background contents and diagrams of anomalies. This whole set of materials has several areas of application.

Firstly, they are a kind of benchmark characterizing the landscapes of the water area and the level of concentrations of chemical elements in silts and water for the testing period, and thus create the basis for qualitative and quantitative monitoring.
Secondly, these materials make it possible to identify anomalies of chemical elements in silts that require special attention when assessing the state of the environment and the approach to determining the quality of nature management in the future.

Thirdly, on the basis of background and abnormal contents of different levels of contrast (it is advisable to have at least three levels), it is possible to develop standardizing values and then use them to assess the degree of deviation of the contents detected during control testing from the calculated value in order to objectively determine the quality of management or the extent of the damage caused.

Fourthly, the information collected will help determine the list of priority regional and local indicators (including federal ones) subject to mandatory control.

Fifthly, the results of the study will be the basis for the development of further nature conservation activities and adjustments of nature management in the water area and coastal zone.

Sixthly, the accumulated materials make it possible to assess the assimilation capacity and resistance of ecosystems to various types of impacts, the possibility of biodegradation or neutralization of pollution agents, the degree of their accumulation in the landscape, or a quantitative assessment of the removal rate.

The use of geochemical landscape maps is also advisable when interpreting the results of ecological studies, since many populational or epidemiological variations in the biosphere are caused by changes in the contents and ratios of chemical elements in the landscape.

7. Conclusion

Thus, the anthropogenic impact and the flow of chemical elements into water bodies in some cases leads to the appearance of geochemical anomalies and, in others, to a change in the aquatic landscapes themselves.

Most often, due to anthropogenic runoff, the input of various biogens increases, eutrophication of water bodies develops, the amount of organic matter increases, oxygen deficiency aggravates, the oxidative conditions are replaced by the gleys, and in sea waters also by the hydrosulfuric ones. This leads to precipitation of most heavy metals from solution and their concentration in the bottom layers of water and further in the silts. This is accompanied by the accumulation of technogenic suspended matters at the bottom and the transformation of transaquatic and transaccumulative landscapes on sands and aleurites into accumulative ones on fine aleurite or clayey silts. As a result, aeration decreases, the sorption capacity of silts grows sharply and the concentration of pollution increases.

As a result of the close interconnection of various components of water bodies, as well as the specificity of anthropogenic impact on water resources, including ship power plants in the process of navigation [9, 10], man-made and natural transformation of landscapes does not occur arbitrarily, but according to a certain scheme. This allows modeling specific consequences on any part of a river or sea when factors affecting the development of aquatic landscapes change.

Aquatic landscapes, like terrestrial ones, have an unequal ability to concentrate matter and change under the influence of anthropogenic factors. They have different resistance to anthropogenic impact, which is understood as the ability to resist anthropogenic transformation and is defined as assimilation potential [8].

All this makes it possible to use the results of geochemical studies and mapping of aquatic landscapes for assessing and monitoring the state of water resources, determining indicators of environmental regulation (parameters of the background and anomalous distribution of chemical elements in silts of various landscapes), modeling the results of anthropogenic impact and establishing the assimilation potential.

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