AQUATIC ECOSYSTEM AND IMPROVEMENT OF WATER QUALITY: WATER SELF-PURIFICATION

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ABSTRACT. *A new analysis of author's data on ecotoxicology and biological effects of synthetic surfactants, detergents and other chemical pollutants helped to formulate an innovative theory of water self-purification in aquatic ecosystems. Fundamental elements of this theory were presented and revisited in this article. In addition to this theory, a discussion of transformations of chemical pollutants is presented. Author's experiments discovered new facts on how chemical pollutants can decrease water self-purification as exemplified by water filtration by aquatic organisms.*

Keywords: water quality, water self-purification, ecotoxicology, surfactants, detergents, aquatic ecosystems, pollution control

1. INTRODUCTION.

In this article, in a condensed form the basic elements are generalized and systematized of the theory of the multifunctional role of the biota in improving water quality, in the self-purification [1–6] and ecological remediation [7] of aquatic ecosystems using the results of previous analyses [3, 4, 7, 8-14] and the theory of the functioning of aquatic ecosystems [2]. It is expected that on the basis of this theory some efficient ecotechnologies will emerge to remediate and restore polluted aquatic systems. The paper is based on the presentations that the author made at scientific seminars in the V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, and at the conferences of the series 'Aquatic Ecosystems and Organisms'. The paper is based on several previous author's publications including those in refereed journals: "Ecologica" (Republic of Serbia), "Russian Journal of General Chemistry", "Doklady Biological Sciences", and other publications.

2. FORMATION OF WATER QUALITY: THE MAIN PROCESSES OF WATER PURIFICATION IN AQUATIC ECOSYSTEMS.

Many physical, chemical, and biotic processes are important for the formation of water quality and water purification in aquatic ecosystems [1–6]. Earlier the author published the list of these processes; a revised list of the most important processes and factors is given in Table 1. Many of these physical and chemical processes are either controlled or affected to a certain degree by biological factors. For example, (1) the rate of the sorption of pollutants by settling particles of suspensions depends on the concentration of phytoplankton cells; (2) photo-chemical decomposition of substances is only possible in transparent water, and the transparency is ensured by the filtration activity of aquatic organisms (hydrobionts that are filter-feeders). Thus, biotic processes are pivotal for the entire system of water self-purification.

3. THE MAIN FUNCTIONAL BLOCKS OF THE SELF-PURIFICATION BIOMACHINERY OF AQUATIC ECOSYSTEMS

Let us distinguish the following main functional blocks covering the major part of the entire biological mechanism of the self-purification of aquatic ecosystems: (1) filtration activity or "filters"; (2) mechanisms of transferring or pumping chemical substances between ecological compartments (from one medium to another); and (3) degradation of pollutant molecules.

3.1. Filters (see also [4, 17]). The following functional systems can perform the function of filters:

(a) the aquatic invertebrates that are filter feeders [18];

(b) aquatic plants (macrophytes), which take up part of nutrients (N, P) and pollutant substances entering the ecosystem from adjacent areas;

(c) benthos (the community of bottom-located organisms), which takes up and consumes some part of nutrients (nitrogen N, phosphorus P) and pollutant substances that can migrate at the water–bottom sediment interface;

and

(d) microorganisms adsorbed on suspended particles moving relative to the mass of water due to the sedimentation of the particles caused by gravity; as a result, the mass of water and the microorganisms move relative to each other, which is equivalent to the situation where water is filtered through granular substrate with attached microorganisms, the latter remove a part of dissolved organic compounds and nutrients (N, P) from the water [4].

3.2. Mechanisms of transferring of pumping chemical substances from one ecological compartment to another (pumps). The following functional systems may serve as pumps:

(a) Sedimentation of particles through a water column: the functional pump facilitating the transfer of part of pollutants from the water into sediments (sedimentation and sorption are involved);

(b) Evaporation: the functional pump transferring part of pollutants from the water to the atmosphere;

(c) Migration of organisms from water: the functional pump determining the transfer of part of nutrients (the compounds that contain N, P) from the water to the surrounding terrestrial ecosystems; examples are provided by all migrations of organisms related to the emergence of imago insects whose larval development to occurs in water; the biomass of the bodies of these organisms contains some amount of chemical elements including nitrogen (N) and phosphorus (P); other examples of migration of organisms can be also considered as factors to transfer of chemical elements;

and

(d) a similar functional pump transferring part of nutrients from water to the surrounding terrestrial ecosystems because of some birds' feeding on aquatic organisms (hydrobionts): e.g., fish-eating birds remove biomass from the aquatic ecosystem; they inhabit the areas adjacent to the water bodies or streams.

3.3. Decomposition of pollutants ("mills"). The functional systems decomposing pollutants are (a) the "mill" of intracellular enzymatic processes;

(b) the "mill" of extracellular enzymes that are present in water;

(c) the "mill" of photochemical processes sensitized by substances of biological origin; and

(d) the "mill" of free-radical processes involving ligands of biological origin (Yu. I. Skurlatov, cited in: [4]).

3.4. Sequestration of pollutants. In addition to the three groups of processes mentioned above, we consider sequestration or immobilization of pollutants by aquatic organisms or by biogenic organic matter as other important processes to remove pollutants from water. The accumulation of heavy metals by aquatic organisms is an important example. E.g., the accumulation of heavy metals by plants and bivalves is well documented. We have performed and currently we run new experiments to further characterize the processes of metal (Cu, Fe, Cd, Zn, Co, Mo, Ni and others) uptake and accumulation by aquatic organisms, namely, bivalves (freshwater mussels *Unio pictorum*, and others). In our experiments, the author has found relevant new facts on immobilization of chemical pollutants by biogenic material including detritus.

4. ENERGY SOURCES OF THE BIOTIC MECHANISMS OF AQUATIC ECOSYSTEM SELF-PURIFICATION

Ecosystems receive energy for biotic self-purification from photosynthesis, oxidation of autochthonous organic compounds, and other redox reactions. Thus, almost all available sources of energy are involved.

Some energy is obtained from the oxidation of the components (dissolved and suspended organic matter) that have to be removed from the ecosystem. In other words, the energetics of self-purification resembles energy-saving technologies invented by engineers.

5. THE ROLES OF THE MAIN LARGE TAXA IN AQUATIC ECOSYSTEM SELF-PURIFICATION

Microorganisms, phytoplankton, higher plants, invertebrates, and fish are involved in the self-purification of aquatic ecosystems and the formation of water quality [4, 8, 10, 12]. Note that each of these groups is involved in more than one or two process (see Table 1 in [7] for details). All of these groups are almost equally necessary for normal self-purification.

E. g., we are currently running a new series of experiments that help to elucidate the potential of aquatic plants (macrophytes) to remediate the polluted water. In our group, the graduate student E.A. Solomonova conducted innovative experiments that quantified the ability of several species of macrophytes (*Elodea canadensis*, *Potamogeton crispus*, *Salvinia* sp. and some others) to remediate the aquatic environment polluted with organic pollutants.

6. RELIABILITY OF WATER SELF-PURIFICATION SYSTEMS

In technology, the reliability of a system is often ensured by doubling many components of the system. Analysis of the functions of ecosystems shows that they employ the same principle. For example, the filtration activity of aquatic organisms (hydrobionts) is doubled (duplicated): it is performed by two large groups of organisms: the plankton and the benthos. Both groups filter water rapidly [1, 5].

Benthos also additionally doubles the activity of planktonic organisms residing in the pelagic zone, because the larvae of many benthic filter-feeders are components of plankton. In the plankton, two groups of invertebrate multicellular filter-feeders, crustaceans [5] and rotifers [4, 6] duplicate (double) each other’s functions of water filtration. Another large group of organisms with a different type of nutrition, protozoa, also filters water as crustaceans and rotifers do. Some other organisms also filter water (for the list of these, see Table 3 in [12]).

Enzymatic decomposition of pollutants, another component of water self-purification, is simultaneously performed by bacteria and fungi. Almost all hydrobionts that, to different extents, can take up and oxidize dissolve organic compounds also fulfill this function (although the activity of each group of organisms has certain specificity).

Thus, the reliability of water self-purification in ecosystems is ensured by the multiplicity of the processes involved, which are performed simultaneously and secure each other’s function. In turn, water purification and permanent restoration (repair, upgrading) of its quality is among the most important elements of the self-sustaining stability of the entire aquatic ecosystem.

The permanent recovery of water quality is absolutely necessary for the stability of ecosystems, because it constantly withstands the constant inflow of autochthonous and allochthonous organic compounds and nutrients (including substances that contain N and P) carried from the adjacent land and tributaries (by water currents), as well as by precipitation and settling waterborne particles. Therefore, water self-purification is as crucial for the stability of ecological systems as DNA reparation (repair) is for heredity; therefore, water self-purification may be regarded as ecological reparation (repair) of aquatic ecosystems [7]. Another important element of the reliability is biota self-regulation.

7. REGULATION OF SELF-PURIFICATION.

Almost all organisms involved in intense self-purification activity are under the double control of the preceding and the next links of the food chain. Earlier [9, 17], the author proposed inhibitory analysis of regulatory interactions in food chains as an effective method for studying the regulatory functions of different organisms.

Various types of signals, including chemical information carriers, play considerable roles in the regulatory mechanisms of ecosystems. It has been suggested that these chemical substances be termed ecological chemoregulators and ecological chemomediators [3].

The influence of regulatory factors on the organisms involved in water quality self-restoration explains why the observed rates of some self-purification processes are considerably lower than the maximal rate that the hydrobionts are capable of. For example, the rate of water filtration in natural water bodies is not high enough to remove suspended organic matter from the water. In many filter-feeders, the filtration rate has been demonstrated to decrease with an increase in the concentration of sestonic particles [5].

8. THE RESPONSE OF THE ENTIRE SELF-PURIFICATION SYSTEM TO EXTERNAL FACTORS AFFECTING AN ECOSYSTEM.

The system of self-purification and water quality formation is labile (easily changeable) [4, 8, 10] and is readily rearranged as the environmental condition change, which makes it difficult to determine its general functional patterns. Experiments of the author [4, 8, 10, 17] have demonstrated the existence of an important element of the vulnerability of a specific process, namely, the process of water filtration by hydrobionts (mollusks and rotifers). This is exemplified by the results of our experiments on the treatment of the mollusks, marine mussels *Mytilus edulis* and *M. galloprovincialis*, and the rotifer *Brachionus calyciflorus* with a synthetic surfactant, tetradecyltrimethylammonium bromide (TDTMA), and synthetic detergents. Our experiments proved that these filtration processes were inhibited by *sublethal* concentrations of man-made chemical pollutants, namely, surfactants and surfactant-containing mixed preparations.

We have published new data on similar inhibitory effects of various chemical pollutants (including synthetic surfactants and detergents) on mollusks and zooplanktonic filter feeders [4, 19, 20, 21]. These data (Table 2; see [4, 21] for the experimental methods) demonstrate that a decrease in the effectiveness of the self-purification (ecological remediation) system of the water is hazardous under the conditions of anthropogenic impact on aquatic ecosystems [4, 7, 17]. In addition to the data presented in Table 2, we have recently shown that some other pollutants inhibit water filtration by filter-feeders. Several heavy metals (not only Cu, but also Cd, Cr, Co as well as other chemical elements) are among those pollutants (S.A. Ostroumov, new data, in preparation).

9. AN AQUATIC ECOSYSTEM AS AN ANALOG OF A BIOREACTOR WITH A WATER PURIFICATION FUNCTION.

The specific features of the water self-purification system invite analogies with a bioreactor. This analogy seems attractive and substantiated. However, it illustrates only one essential aspect of aquatic ecosystems. It is justified and useful in certain respects [8]; however, it by no means reflects comprehensively the essence of aquatic ecosystems, with all their diversity and variability.

In our analysis, it is possible to apply one of scientific terms that were often used by the prominent Russian scientist, who was ahead of his time, V.I. Vernadsky (1863-1945, one of the fathers of biogeochemistry), namely the word ‘bioinert’. The word ‘bioinert’ in transliteration of the original Russian word is ‘biokosny’. This unique word means an integral combination of biotic and abiotic factors. The regulation of many important processes involved in the transfer of chemical elements in aquatic ecosystems is bioinert, i.e., combines the effects of biotic and abiotic factors. It seems useful to pay attention to the *bioinert nature* (in transliteration of the original Russian word combination is: 'biokosnaya priroda', it means summation and integral unity of biotic and abiotic factors) of the regulation of the transfer of chemical elements in aquatic ecosystems. Using this terminology helps to emphasize the significance of both biotic and abiotic factors as equally important and interacting factors that regulate the movement of chemical elements and mass transfer in water bodies and streams.

Aquatic ecosystems are characterized by considerable variability of almost all main parameters. In these systems, an almost complete absence of constant quantitative characteristics is noticeable.

We consider some analogy between aquatic ecosystem and a multifunctional bioreactor, but we understand that the analogy with a technological device is limited and not complete. With this important caveat, we may conclude (again, with some reservations) that the system of processes involved in the self-purification of an aquatic ecosystem is similar to a high-technology device and may be regarded as a bioreactor fulfilling functions that are important for the ecosystem. However, this analogy involves only one essential aspect of an aquatic ecosystem.

10. IMPLICATIONS FOR ENVIRONMENTAL PROTECTION AND ECOLOGICAL ENGINEERING.

Taking into account the theory described above, as well as the results of my earlier experimental studies [7, 8, 12, 13, 17] and data published by other researchers [1, 5, 6], the author consider possible to formulate the following notions and recommendations. It is possible that they could be useful for mitigation some issues related with the protection of biodiversity and environment.

(1) The conservation of the self-purification capacity of water bodies and water streams should be an essential element of environmental protection programs [13], and of projects to remediate and restore polluted or damaged aquatic ecosystems.

(2) Almost all species of hydrobionts are involved in the formation of water quality and self-purification of aquatic ecosystems or the regulation of these processes. This is one more argument in support for the conservation of the entire biodiversity in aquatic ecosystems [12].

(3) Many of organisms that are part of the terrestrial ecosystems adjacent to water bodies and water streams are largely involved in water purification; therefore, the conservation of biodiversity in these coastal terrestrial ecosystems is also necessary for sustaining the quality of water [13].

(4) The environmental protection measures and regulations in the protected terrestrial and aquatic areas should include not only the conservation of populations and gene pools, but also the maintenance of the functional activity of these populations (specifically, the functional activity that contributes to the maintenance of water quality and, hence, the stability of the entire ecosystem) [13].

(5) New hazards related to the chemical pollution of aquatic ecosystems have been identified [7].

(6) When solving the problem of the eutrophication of aquatic ecosystems, my earlier suggestions on the synecological approach should be taken into account [11].

(7) The assessment of the anthropogenic damage to the environment should take into account, among other factors, the damage due to the decrease in the self-purification capacity of water bodies and waterways. This brings a new element into the interpretation of environmental legislation, including both international laws and regulations and the national environmental legislation.

(8) The theory offers a new approach to a more comprehensive economic assessment of the anthropogenic damage to aquatic ecosystems and organisms involved in the self-purification of aquatic ecosystems [14].

(9) According to the theory described above, we may expect new examples of chemicals hazardous for the capacity of aquatic ecosystems for self-purification.

(10) The theory presented above arrange a broad diversity of facts on how various organisms assist each other in cleaning water and up-grading water quality. The theory may help to develop efficient projects that involve bioremediation, phytoremediation and other types of ecotechnologies to clean aquatic systems including water bodies and water streams. The author used this theory in developing elements of new phytotechnologies for water purification. Several studies were published (some of them coauthored with the graduate student, E.A. Solomonova).

11. VERIFICATION OF AND SUPPORT FOR THE THEORY FROM THE STUDIES OF VARIOUS AUTHORS

A number of additional studies by other authors and by the author of this paper gave additional support to the theory presented above.

Examples of publications of international researchers who mentioned abovementioned results of analysis of ecosystems and ecotoxicological hazards of chemical pollutants are the articles [22-32].

Some other publications of the author of this paper provided more facts and considerations in support of the author’s theory of biotic water self-purification [33].

12. FINAL COMMENTS AND CONCLUSION.

We consider what is said above as elements of theory of improving of water quality – or, in other words, the theory of biomachinery of water self-purification. If we consider the pathways of molecules of pollutants and of their transformations and migrations within aquatic ecosystems and organisms, we may see an analogy with pathways of

.Table 1. Some key processes and factors performing a role in purification, remediation and upgrading the quality of water in aquatic ecosystems. In reality many of these processes and factors are overlapping.

Types	Processes and factors
1. Physical	1.1 Dilution. 1.2 Adsorption. 1.3 Sedimentation. 1.4 Evaporation.
2. Chemical	2.1 Hydrolysis. 2.2 Photochemical reactions. 2.3 Oxidation. 2.4 Free radical-dependent destruction. 2.5 Sorption or related types of immobilization. 2.5 Complexation by and binding to other molecules.
3. Biological	3.1 Organism-dependent oxidations and biotransformations. 3.2 Transformations performed by enzymes excreted into aquatic medium. 3.3 Accumulation by organisms, incorporation into biomass. 3.4 Filtering of water by filter-feeders and suspension-feeding organisms. 3.5 Excretion of molecules which are instrumental in increasing the rate of some chemical processes of degradation of pollutants (e.g. photodegradation). 3.6 Excretion of organic molecules which are instrumental in decreasing the toxicity of pollutants as a result of binding of the pollutants to those organic molecules. 3.7 Producing oxygen that is involved in chemical oxidation of pollutants. 3.8 Regulation of biological processes of water purification by other organisms.

Table 2.: Some chemicals that have an inhibitory effect on the filtering activity of the marine filter-feeders. As a result, the amount of suspended matter removed from the water by the filter-feeders decreased. Therefore the amount of suspended matter left in the water was more than that in control. Original data of the author. The method described in [7, 21]. Abbreviations used in the table: LD – liquid detergent; SD - synthetic detergent; SDS - sodium dodecylsulfate (a synthetic surfactant); TDTMA - tetradecyltrimethylammonium bromide (a synthetic surfactant)

Measurement No.	Chemical (described in the text)	Concentration of the chemical, mg l^{-1}	Organisms	Effect of the chemical (the ratio of the concentration of suspended matter in the system with the chemical to that in the control), %
1.	heptane	16	Marine mussels *Mytilus galloprovincialis*	209.1
2.	$CuSO_4 \cdot 5H_2O$	2	Marine mussels *Mytilus galloprovincialis*	140.0
3.	surfactant TDTMA	0.5	oysters *Crassostrea gigas*	344.2
4.	synthetic detergent SD1 (laundry detergent 'Lanza')	20	oysters *Crassostrea gigas*	261.7
5.	liquid detergent LD2 ('Fairy')	*2*	Marine mussels *Mytilus galloprovincialis*	218.8
6.	liquid detergent LD2 ('Fairy')	*2*	oysters *Crassostrea gigas*	1790.0
7.	synthetic detergent SD2 (laundry detergent 'IXI')	*10*	Marine mussels *Mytilus galloprovincialis*	157.8
8.	synthetic detergent SD3 (laundry detergent 'Deni')	*30*	oysters *Crassostrea gigas*	5800.0
9.	surfactant Triton X-100	*1*	Marine mussels *Mytilus edulis*	236.2
10.	Triton X-100	*4*	Marine mussels *Mytilus edulis*	1505.6
11.	surfactant SDS	*1*	Marine mussels *Mytilus edulis*	271.1
12.	SDS	*4*	Marine mussels *Mytilus edulis*	1473.2

metabolism of molecules inside cells. What is common is the complexity of pathways, many transformations of the molecules, and the vital role of biotic processes. On the basis of that analogy we propose to consider the traditional term 'metabolism' as inner metabolism or endometabolism. By contrast, we propose to consider the pathways of molecules in the aquatic medium of ecosystems as external metabolism or exometabolism. If we accept the terms endometabolism and exometabolism, we can consider their sum as the integral metabolism of pollutants in aquatic ecosystems.

Using the proposed terminology, we can consider the entire material of this paper as elements of the theory of the integral metabolism of pollutants. This is an explanation for the title of the paper.

All in all, the results of the analysis performed allows the community of aquatic organisms to be regarded as a device for ecosystem self-purification – a device that constitute an essential part of what V.I. Vernadsky (1863-1945, one of the fathers of biogeochemistry) called the "biosphere apparatus." The notions put forward in this paper have further developed and detailed some of V.I. Vernadsky's concepts (on the biogenic migration of chemical elements, and the biosphere apparatus).

13. SUMMARY.

Fundamental elements of a new theory for the biological mechanism for water self-purification are presented. Aquatic organisms are actively involved in various processes leading to water purification. Not only microorganisms (bacteria, cyanobacteria and fungi), but also algae, plants, invertebrates, and many other groups of organisms are involved, which is discussed and analyzed in the paper. Results of the author's experiments that study the effects of various pollutants on aquatic organisms (freshwater and marine bivalve mollusks) are given. The theory is an innovative basis for developing ecological technologies to clean water and to upgrade its quality by using organisms and ecosystems

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