ISSN 1995-4255, Contemporary Problems of Ecology, 2008, Vol. 1, No. 1, pp. 147–152. © Pleiades Publishing, Ltd., 2008.
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Basics of the Molecular-Ecological Mechanism of Water Quality Formation and Water Self-Purification

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Abstract—The paper formulates some basics of the modern ecological theory of the polyfunctional role of biota in the molecular-ecological mechanism of water quality formation and self-purification of aquatic ecosystems. The theory covers the following items: (1) sources of energy for self-purification mechanisms, (2) the main structural and functional units of the self-purification system, (3) the main processes involved in the system, (4) contributions of major taxa to self-purification, (5) system reliability and supporting mechanisms, (6) the response of the system as a whole to external factors, (7) particulars of the operation of water purification mechanisms, and (8) conclusions and recommendations for biodiversity preservation practice.

DOI: 10.1134/S1995425508010177

Water quality formation and self-purification of aquatic ecosystems involve numerous physical, chemical, and biotic processes ([1–5], see also references to Ivanova, 1976; Konstantinov, 1979; Kokin, 1981; Skurlatov, 1988; et al. in [6]). The interaction of these processes forms a molecular-ecological mechanism [7–14]. The operation of this mechanism is part of the operation of an aquatic ecosystem [2, 15–17]. The theory of aquatic ecosystem operation is being developed by Alimov [2].

This article summarizes notions on the role of biota in the molecular-ecological mechanism of water quality formation and self-purification of water basins and watercourses. This synthesis is performed at the basic level without complete reviewing all studies in this vast field of research.

1. The sources of energy for the operation of the molecular-ecological mechanism of water quality formation and water self-purification are: photosynthesis, oxidation of autochthonous and allochthonous organic matter, and other redox reactions. Thus, virtually all available energy sources are employed. It is worth noting that part of the demanded energy is obtained by oxidation of the components the system eliminates. In other words, self-purification processes can be compared to energy-conservative technologies [8].

A quantitative example is Lake Mirror, USA. The following annual amounts of carbon (g C/m^2) are oxidized there by various groups of organisms: phytoplankton, 1–9.1; zooplankton, 12.0; macrophytes, 1.0; sessile algae, 1.16; benthic invertebrates, 2.8; fish, 0.2; bacteria in bottom sediments, 17.3; and bacterioplankton, 4.9 [4, p. 772].

2. The main structural and functional units of the mechanism supporting water quality, whose assembly covers a significant portion of the general hydrobiological mechanism of aquatic system purification [17], are those responsible for:

(1) filtration ("filters") [9],

(2) transfer of chemicals between ecologic compartments (between econiches) ("pumps"); and

(3) pollutant degradation ("mills").

Filters are considered in detail in [9]. The following functional systems of filtration can be recognized: filtering aquatic organisms; the belt of bank macrophytes, entrapping part of biogens and pollutants supplied to the ecosystem from the neighboring land; benthos, entrapping and consuming part of biogens and pollutants migrating at the water/bottom sediment interface; and microorganisms attached to suspended particles migrating relative to the waterbody [9].

Pumps. The following functional systems perform the transport of pollutants [17]: sedimentation and adsorption (from the water column to sediments), evaporation of part of the pollutants (from water to the atmosphere), and migrational processes related to emergence of insect imagos from waterborne larvae and to the feeding of birds consuming biomass from water areas but nesting on terrestrial areas adjacent to the waterbody or watercourse (from water to adjacent terrestrial areas). The removal of large amounts of autochthonous organic matter produced by phytoplankton in the course of photosynthesis is of great significance for aquatic ecosystem self-purification. This removal is greatly contributed by the process often referred to as the biological pump: zooplankton-mediated removal of part of the phytoplankton from the photic layer of the water column. Zooplankton excretes the unassimilated organic matter in the form of pellets. These pellets descend to deeper water column layers owing to gravity. This process is another type of functional pump, significant for description of the operation of oceanic ecosystems. It is more or less significant for all deep-water ecosystems.

Mills include the following mechanisms, according to [17]: enzymatic processes, photochemical processes sensibilized with substances of biological origin, and free-radical processes involving biological ligands (see also Skurlatov et al. 1983 and Skurlatov et al. 1988 cited in [6]).

Many quantitative studies of the corresponding processes have been reported. Lake Mirror loses 0.5 g C/m^2 annually owing to insect imago emergence, which constitutes 0.6% of the supply of auto- and allochthonous organic carbon [4, p. 772]. Photolysis of natural water containing 10 mg of dissolved organic carbon per liter generates levulinic acid (more than 1 mg C/l) after 240 min irradiation [4, p. 762].

3. The main physical, chemical, and biotic processes essential for the molecular-ecological mechanism of water quality formation are discussed in our reports [6, 8, 10]. These processes are summarized here in Table 1. It is important that the key role in water quality formation and water self-purification is played just by biotic processes 3.1–3.15 (considered in detail in [4, 8–13]. The presence of biotic processes in mechanisms of water quality formation and self-purification poses questions of what taxa are involved in this mechanism and to what extent this mechanism is reliable and vulnerable.

4. Assessment of the involvement of main high-level taxa in self-purification. The role of major high-level taxa in water system self-purification was analyzed in our paper [10]. Microorganisms, phytoplankton, higher plants, invertebrates and fishes were considered. All these groups are involved in water ecosystem self-purification. Each of them is involved in more than one or two processes, and all of them are equally important for the proper operation of the self-purification mechanism.

Quantitative evaluations of the contributions of different processes are broadly variable among ecosystems. Eutrophic Lake Esrom (Denmark) is an example of such evaluation in percentage of the total removal of carbon from water: respiration of producers, 24.4; bacterial respiration, 20,9; secondary respiration (respiration of consumers), 30.7; respiration of organisms in sediments (may be incompletely determined), 4.5; chemical oxidation in sediments, 3.4; carbon binding in secondary products, 11.9; emergence of aquatic insect imagos, 0.14; accumulation in bottom sediments, 2.8; and export of soluble and suspended carbon forms with water current, 0.8 (according to Jonasson et al., 1990, as cited in [4, p. 707].

5. The reliability of the system and the mechanisms supporting it are related to duplication of many system components. For example, two major groups of aquatic organisms, plankton and benthos, are involved in filtration activity. Both groups filter water at significant rates [3, 6]. Benthos duplicates the action of plankton because larvae of many filter-feeding benthic organisms have a planktonic life habit. Plankton includes two major groups of filter-feeding invertebrates: crustaceans and rotifers, which duplicate each other. In addition, protozoans, another group with a different feeding habit, duplicate the filtration activity of filtering multicellular animals.

The function of enzymatic degradation of pollutants is partly duplicated by bacteria and fungi. Oxidation of dissolved organic matter is duplicated by virtually all aquatic organisms, more or less able to absorb and oxidize DOM, although the activities of particular organism groups have specific features.

Another important component of system reliability is biota self-regulation. Virtually all organisms intensely performing processes involved in water self-purification experience double control by organisms of the preceding and subsequent trophic levels. The regulating role of these organisms can be successfully studied by the method proposed by us in [11]: inhibitory analysis of regulatory interactions in trophic chains.

Some quantitative indices broadly variable among ecosystems can be illustrated by the example of filtration evaluation. In terms of body volumes per hour, this activity reaches $5 \cdot 10^6$ for nanoflagellates and $5 \cdot 10^5$ for ciliates according to Penchel (1986, 1987) as cited in [4]. For cladocerans, this index is 4–6 (seldom reaching 14) ml per animal per day according to many studies cited in [4]; according to other publications cited in [1], 20–40 (seldom reaching 130) ml/animal/day. For copepods, 2–4 (seldom to 27) ml/animal/day (ibid., p. 423); for rotifers, to 0.3 ml/animal/day (typically, to 0.07–0.17 ml/animal/day) [3].

However, the Nature has not provided for the appearances of anthropogenic influence on the biosphere or prepared itself for defense against this influence. A question arises as to the response of the machinery of water quality formation and individual components of this machinery to anthropogenic influence.

6. Response of the mechanism of water quality formation and water self-purification to anthropogenic influence. Generally, this mechanism is labile and readily adjustable to environmental changes. This hampers the study of general regularities of its operation. Lability of a particular process involved in self-purification, namely, water filtration by aquatic animals (mollusks and rotifers) has been demonstrated in our experimental studies [6–14]. These processes were inhibited by sublethal concentrations of pollutants: some metals, surfactants, surfactant-containing mixtures, and other xenobiotics (Table 2). The metal salts reducing the filtration activity of mollusks include lead, cobalt, copper, and others (Table 2). In my experiments, the concentrations of lead, cobalt, and copper salts reducing the filtration activity of mussels were sublethal, i.e., they did not cause mollusk death. Similar studies with mercury salts (mercury sulfate, 10 mg/l) caused mollusk death. My recent studies have demonstrated inhibition of water filtration by mollusks with the presence of titanium (potassium titanofluoride) and vanadium (sodium orthovanadate, $Na_3VO_4 \cdot 12H_2O$) salts.

Table 1. Some factors and processes involved in the molecular ecological mechanism of water quality formation as compiled from studies by many scientists

No.	Water purification factors and processes
1	PHYSICAL AND PHYSICOCHEMICAL
1.1	Dissolution and dilution
1.2	Carryover to the banks
1.3	Carryover to adjacent water basins and watercourses
1.4	Adsorption by suspended particles followed by sedimentation
1.5	Adsorption by bottom sediments
1.6	Evaporation
2	CHEMICAL
2.1	Hydrolysis
2.2	Photochemical conversion of DOM and pollutants
2.3	Catalytic redox conversion
2.4	Pollutant conversion induced by free radicals
2.5	Decrease in pollutant toxicity owing to binding to DOM
2.6	Oxygen-mediated chemical oxidation of pollutants
3	BIOTIC
3.1	Adsorption and accumulation of pollutants, DOM, and biogens by aquatic organisms
3.2	Pollutant bioconversion: redox reactions, degradation, and conjugation
3.3	Extracellular enzymatic conversion of pollutant and DOM molecules performed by enzymes dissolved in the water of natural basins and watercourses (exoenzymes) and enzymes immobilized on interfaces in aquatic ecosystems
3.4	Removal of suspended particles from the water column by water filtration by aquatic organisms
3.5	Removal of suspended particles from the water column by adsorption on pellets excreted by aquatic organisms
3.6	Arrest or retardation of the supply of biogens and pollutants from bottom sediments to the water column; accumulation and binding of biogens and pollutants by benthic organisms
3.7	Carryover of C, N, and P from the ecosystem with aquatic insect imagos (*Plecoptera, Ephemeroptera, Odonata, Trichoptera, Diptera*, etc.)
3.8	Production of allelopathic and bactericidal substances and their excretion to water
3.9	Carryover of C, N, and P from the ecosystem in the course of nourishment of fish-feeding and other predatory animals living in areas adjacent to the water basin
3.10	Carryover of C, N, and P from the ecosystem with amphibians leaving water for land in the course of metamorphosis
3.11	Release of hydrogen peroxide by algae, which is essential for pollutant conversion by redox reactions
3.12	Excretion of substances participating in photochemical degradation of chemicals and pollutants (photosensibilizers and their precursors)
3.13	Excretion of substances essential for free-radical-mediated degradation of chemicals (organic ligands and their precursors)
3.14	Excretion of organic substances participating in formation of an organic surface film regulating heat and matter transport between the basin and atmosphere (for details, see [19])
3.15	Bioconversion and adsorption of pollutants in soil during field watering with polluted water
3.16	Further fragmentation of large organism fragments supplied to the basin by aquatic animals
3.17	Regulation of the population and activity of organisms involved in water purification by interactions between organisms

Note. Many factors are related to each other and are superimposed. It is often impossible to isolate individual factors, and this division is performed mainly for the sake of conceptual analysis.

DOM, dissolved organic matter

Table 2. Recent data on the disturbance of water filtration as part of its self-purification under the action of pollutants. Action of various pollutants on the removal of suspended matter from water by filter-feeding organisms. The degree of suppressing activity of chemicals (effect on the efficiency of suspension removal, EESR) was calculated as in [6]

No.	Substance	Organism	Concentration, mg/l	Notes and references
1	Triton X-100	Swollen river mussel *Unio tumidus*	5	Ostroumov, 2001a [6]
2	Trimethyltin chloride	*Dreisseria polymorpha*	0.01–10	Mitin, 1984, cited in [6]..
3	Lindane	*Mytilus edulis*	0–1.5	Donkin et al., 1997, cited in [6]
4	Dichlorvos	The same	0–1	Ibid.
5	Cadmium sulfate	*M. galloprovincialis*	0.5	My recent results
6	Copper sulfate	The same	2	The same.
7	Lead nitrate	The same	20	The same.
8	Mercury sulfate $HgSO_4$	The same	10	The same.
9	Cobalt sulfate $CoSO_4 \cdot 7H_2O$	The same	18–53	The same.
10	TDTMA	*M. edulis* × *M. galloprovincialis* (natural hybrid population)	0.05–5	Recent results
11	TDTMA	*Crassostrea gigas*	0.5	EESR 761% (recent results)
12	SDS	*M. edulis* and *M. galloprovincialis*	>1	[6]
13	SDS	*Crassostrea gigas*	0.5	EESR 231% (recent results)
14	Triton X-100	*M. edulis*	≥1	[6]
15	Detergent OMO	*Unio tumidus*	50	EESR 187% [6]
16	Detergent Tide	*M. galloprovincialis*	50	EESR 207% [6]
17	Detergent Losk	The same	7	EESR 551% [6]
18	Detergent IXI	The same	10	EESR 158% [6]
19	Detergent IXI	The same	50	EESR 276% [6]
20	Liquid detergent E	The same	2	EESR 214% [6]
21	Liquid detergent E	*Crassostrea gigas*	2	EESR 305% [6]
22	Liquid detergent Fairy	The same	2	EESR 1790% [6]
23	Liquid detergent Krasnaya Liniya	*M. galloprovincialis*	60	My recent results
24	Oil hydrocarbons (gas oil)	The same	4–8	The same

Generally, the highest EESR value over the experiment is indicated. Abbreviations: TDTMA, tetradecyltrimethylammonium bromide; SDS, sodium dodecylsulfate.

Evidence for inhibition of water filtration by rotifers was obtained in a new experimental device, turbidostat, where the filtration activity of the rotifers *Brachionus calyciformis* and efficiency of withdrawal of the alga *Nannochloropsis limnetica* (Eustigmatophyceae, 1.5–6 μm in size from the water by these rotifers were constantly recorded. We found a decrease in the rate of alga withdrawal from the medium with the presence of the cationic amphiphilic substance tetradecyltrimethylammonium bromide (TDTMA, 0.5 μg/l) [18].

Thus, our results provide additional evidence for the danger of the reduction of the efficiency of the biological water self-purification (ecological remedy) system caused by anthropogenic action on aquatic ecosystems [6–14, 17, 18].

<u>7. Some basics of the operation of molecular ecological mechanisms responsible for water quality formation and restoration.</u> A set of six principles is recognized. These principles are typically predominant but

not universal because some ecosystems demonstrate deviations from them.

1. Moderation of the rate of water self-purification by regulatory mechanisms. The actual rate of certain processes is in many cases lower than the maximal expected one. This may be related to the action of regulatory mechanisms. It has been noted that if the maximum value of a parameter in an ecosystem does not match its optimum value for organisms, this parameter is likely to undergo self-regulation [19]. For example, the rate of water filtration by aquatic organisms is regulated. It decreases significantly at elevated suspension concentration in water in comparison with the maximum possible rate.

2. Typically, maximal diversification of the executives of the main functions of water quality formation and self-purification machinery is observed. Indeed, as mentioned above, virtually all functions (oxygen release, DOM oxidation and conversion, water filtration, etc.) are duplicated, being performed by multiple species of the ecosystem.

3. Multiple stages of the biogenic migration of elements in the operation of the molecular ecological mechanism of water medium parameter formation are often observed. For example, the carbon atom of a carbon dioxide molecule is involved in a pathway of many stages: It is reduced during photosynthesis by an alga; then it is oxidized in the body of a heterotroph consumer, or it comes to bottom sediments with debris, where it can be oxidized by an aerobic bacterium; then it is reduced again by a methanogenic bacterium to form methane; then it is oxidized by a methanotrophic bacterium; and eventually, this carbon can again be involved in photosynthesis.

4. Synecological cooperation: Many processes participating in the formation of water medium parameter formation and self-purification occur at higher rates and efficiencies owing to cooperation of two or more aquatic species.

5. The significance of biota is constantly preserved at a high level throughout the ecosystem volume and all the time, independently of the time of day, season, and succession stage.

6. Regulated balance of oppositely directed processes. Organisms simultaneously excrete and absorb organic molecules, oxygen, and carbon dioxide; produce suspended organic matter (SOM) and remove it from water by filtration; etc. This fact points once more to the importance of all regulation types, involving biotic and abiotic factors, and emphasizes the danger of anthropogenic distortion of these regulatory mechanisms.

In some respects (continuous operation, importance for maintaining the structure and stability of biologic systems, and pollutant sensitivity), the molecular ecological mechanism of water quality formation and maintenance and restoration of water medium parameters in aquatic ecosystems is similar to reparation mechanisms at other life organization levels.

This article concerns only some components of the complex set of processes and factors involved in water medium parameter formation and water self-purification. Other components of the self-purification machinery are considered in [3, 5, 15, 16, 19].

8. Conclusions and recommendations for environment preservation practice. On the grounds of our experimental studies [8–13], other publications of mine [14], and data published by other scientists [e.g., 3, 4], the following conclusions can be drawn:

1. Virtually all species are involved in processes responsible for aquatic ecosystem self-purification or in regulation of these processes. Distortion of these regulatory mechanisms manifests itself most clearly after invasion of new species into the ecosystems. This provides another argument for the preservation of the whole biodiversity in aquatic ecosystems [14].

2. Species of terrestrial ecosystems and habitats adjacent to water basins and watercourses take an active part in purification processes. Therefore, water quality preservation demands the preservation of the biodiversity of these terrestrial ecosystems as well.

3. The modern concept of biodiversity preservation differs from the previous one, based on the preservation of species gene pool. It follows from the analysis reported in [13, 14] that the biodiversity-preservation tasks and conditions should include not only preservation of gene pools and populations but also preservation of the functional activity of these populations, which contributes to the maintenance of water quality and, as a consequence, the maintenance of stability of the whole aquatic ecosystem.

4. The operation of self-purification machinery in an ecosystem should be taken into account to determine critical anthropogenic loads [15] on the ecosystem and to evaluate the threat of anthropogenic impact on biota [20–22].

5. The self-purification system is important for analyzing the role and fate of most important pollutants, including radionuclides [16], heavy metals [23–25], and other pollutants.

6. The theory under development emphasizes the importance of molecular conversion of pollutants. The poor understanding of this problem is related to blanks in the knowledge of aquatic ecosystems. The filling of these blanks should be given priority to in further studies. They include problems of biochemistry and biophysics of aquatic ecosystems [19, 26]; better knowledge of the biochemical composition of DOM, role and metabolism of particular DOM classes; and determination of concentrations and activities of enzymes dissolved in waters of natural water basins and watercourses (exoenzymes), as well as enzymes immobilized on interfaces in aquatic ecosystems.

Comprehensive analysis of self-purification mechanisms demands a broad range of factual data and consideration of additional sources in scientific literature. More detailed bibliography on the problems touched here is presented in [27–29].

ACKNOWLEDGMENTS

The author is grateful to A. F. Alimov, M. E. Vinogradov, V. L. Kas'yanov, I. Yu. Koropachinskii, V. V. Malakhov, T. I. Moiseenko, E. A. Kriksunov, G. S. Rosenberg, V. D. Fedorov, O. G. Mironov, A. G. Kocharyan, B. M. Dolgonosov, V. M. Khromov, and participants of the conference "Aquatic ecosystems and organisms" (Moscow, 1999–2005) for discussion and remarks. He also acknowledges the assistance of N. N. Kolotilova, J. Widdows, N. Walz, G. E. Shul'man, and other colleagues from the Institute of Biology of the Southern Seas (Sevastopol) in manipulations with filter-feeding animals and sending scientific reprints by M. I. Gladyshev. Part of the experimental studies were supported by the MacArthur Foundation, the Open Society Institute, and Russian Foundation for Basic Research.

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