

Review Article

Reactions' Mechanisms and Applications of Hydrogen Peroxide

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Abstract: Hydrogen peroxide is a key substance in the appearance of life and maintenance of the life-supporting conditions on the Earth. Electron transfer processes between H_2O_2 and various reducers are of major interest for the environment, natural life, technology, etc. An overview of structure, properties and main reactions of hydrogen peroxide in model and real systems is presented. The authors try to find the answers to the following questions: why this substance has the unique and specific dual reduction-oxidation properties, what is the connection between its structure and reactions, what role it plays in the catalytic reduction processes occurring in the natural environment and technological systems, accompanied by the formation of intermediate compounds, active radicals, complete and partial charge transfer complexes, etc. The thermodynamic possibility of the synchronous two-electron transfer during the inner sphere reaction with the involvement of metal ion complexes capable of changing the valence by two units is discussed. The role of the partial charge transfer structures which combine the properties of the initial reagents and the expected reaction products is demonstrated. Such complexes can be decomposed both reversibly and irreversibly. In case when the single-electron transfer is thermodynamically preferable, the main oxidizing particle is OH-radical, capable to interact non-selectively with almost all the water-soluble organic substances. Special attention is paid to the photo initiation of peroxidase transformation processes. The results of our multi-annual research of these issues are reported.

Keywords: Hydrogen Peroxide, Reduction-oxidation, Catalytic Processes, Electron Transfer, Metal Complexes, Water Quality

1. Introduction

This brief review covers a comprehensive material obtained during the long-term research, outlining a new vision on the role of hydrogen peroxide in natural waters and water-containing objects. A new attempt is made to rethink and understand the well-known facts, which lead us to investigate the oxygen cycle in living and environmental systems, including metabolism, self-purification in natural water bodies as well as disinfection of contaminated systems. Hydrogen peroxide is an inevitable component of oxygen cycle.

The main task of this paper is to demonstrate that hydrogen peroxide is not an occasional "intermediate station" on the halfway of oxygen four-electron reduction to water.

Involvement of H_2O_2 in the transformation mechanisms of dioxygen-containing systems is often masked, because the stationary concentration of peroxide is several orders lower than $[O_2]$. The intermediate steps with H_2O_2 participation are inevitable by two reasons. The first is that dioxygen as final product of water oxidation and water itself are so stable and inert, that preliminary activation to reactive oxygen species is needed. The second reason is that simultaneous transfer of four electrons from reductant to oxidizer in polar medium (like water) demands 16-times higher activation energy, as compared to one-electron transfer. Kinetically, two-electron transfer is impossible without intermediate steps of H_2O_2 decomposition.

Some publications regarding hydrogen peroxide, created a negative impression on its role in life processes. It could be

thought that this substance mainly acts as a bactericidal agent, which, if handled carelessly, can kill all the living beings. Certain countries have regulations limiting the maximum

permissible concentrations of H_2O_2 calculated in parts per million [1], which is orders lower than its contents in the most natural systems (Table 1).

Table 1. Some examples of peroxide containing systems.

Natural water-containing system	H_2O_2 concentration, $\mu\text{M/L}$	Reference
Sea water	0.005 - 0.5	David Price et al (1994) [2]
Volga (Russia), Nistru and Prut (Moldova) rivers	0.1 - 3	Fujii, M., & Otani, E. (2017) [3] Cooper et al. (1988) [4]
Ice, snow	0.2 - 2	Andreas Sigg and Albrecht Neftel (1988) [5]
Rain & cloud water	2 - 250	Kenneth J. Olszyna et al, 1988 [6]
Sweet pepper fruits	10 - 600	Sanders Junglee (2014) [7]

The basic principle of nature-regulated objects functioning is homeostasis. Under the undisturbed conditions, the stationary amount of hydrogen peroxide, both inside and outside the cells of living organisms, is constant (although different for different objects types), being determined by generation and consumption rates. Any deviation from the homeostatic value, both increasing and decreasing, affects adversely the organisms' viability. This fact, namely the state with a lack of hydrogen peroxide, has mysteriously escaped from the vision of researchers.

Meanwhile, the lack of H_2O_2 can be even more hazardous than its excess over the maximum permissible concentrations. Its naturally balanced level was "adjusted" by trial and error method over the hundreds of millions of years. This ecological selection was established evolutionarily.

Oxidation and reduction processes are basic processes determining the life origin and existence on the Earth. The early evolution theory is ambiguous and controversial [8], but the most experts agree that proto-atmosphere was free of oxygen. Further, about 2.3 bln years ago, after a 'Great Oxidation Event', it has passed through the two states – reducing and oxidizing [9].

Perhaps it looks strange, but the very first organisms were living due to the oxygenic photosynthesis. The possibility of oxygenic photosynthesis was proved taking as an example the appearance and functioning of the purple bacteria [10]. At that time oxygen contents in the atmosphere was approximately 1/100,000,000, as compared to the present amount [11], therefore, the dissolved hydrogen peroxide was the main biogenic oxidant.

The main reason, why the oxygen producing blue-green algae had won the Evolution competition, is higher solar energy conversion coefficient to biologic matter, than anoxygenic purple bacteria provide. Anyhow, to understand a whole picture, it is important, that counteraction between the opposite flows of oxidizers and reductants always give rise to hydrogen peroxide occurrence, that is the key halfway point between water and oxygen.

The oxygen cycle becomes the fundamental for the biosphere. Within the global biologic circuit, the molecular oxygen is formed in the photosynthetic process of water oxidation and is reduced to water during the oxidative destruction process and elimination of accumulated energy.

The carriers of oxidative equivalents, which are substances with lack of electrons on low energy molecular orbitals, are capable to join electrons. These species include metal ions, oxygen, hydrogen peroxide, free radicals, etc. The reducing

equivalents are substances containing weakly bound electrons, such as enediols, thiols, amines, and polyphenols. The interactions between the oxidants and reductants in natural waters always cause the occurrence of hydrogen peroxide.

"Ontogeny recapitulates phylogeny" – this brief formula of Haeckel's Biogenetic law has received abundant criticism over the past 150 years. Nonetheless, its main idea is still alive [12]. It is strongly believed that fish larvae cannot be developed and switched to active feeding (and breathing) without hydrogen peroxide. The living organisms during the evolution have been adapted to the development only in the oxidative environment, the reducing conditions suppressing them.

An indirect evidence for the evolutionary significance of hydrogen peroxide is that the catalase enzyme has been found in almost all the living organisms. It is responsible for the removal of peroxide excess and prevents the intracellular generation of free radicals. Catalase is one of the fastest-acting enzymes: one catalase molecule can turn millions of H_2O_2 molecules into water and oxygen in a second [13].

It appeared that $[\text{LMn}_2^{\text{II,II}}(\mu\text{-CH}_3\text{COO})](\text{Cl})_4$ complex is one of the best mimetic models of catalase. An important point for the model system is that its active center contains manganese dimer complex [14].

2. Structure and Reactions of Hydrogen Peroxide

This topic have been a subject of the specific interest for the authors of this article and their colleagues for several decades. During this time, the various reaction mechanisms of processes with the involvement of hydrogen peroxide reactions mechanisms in model and natural systems have been studied [15, 16].

The structure of Hydrogen Peroxide molecule has direct impact on its properties. Hydrogen peroxide molecule having a spatial structure [17] can be regarded as a water molecule with one extra oxygen atom. Both oxygen atoms have two pairs of unbound electrons each. This leads to the repulsion of electron clouds and gives a bent molecular shape, with the angle of 109.5° . The single O-O bond between two oxygen atoms is weak, so that H_2O_2 readily decomposes into two O Hs.

Another important specific of this molecule is the rotation of fragments around the O-O bond, only insignificantly limited by the low potential barrier ($\sim 4 \text{ kJ mol}^{-1}$), so dihedral angle between the planes of OH-groups can vary from 90° to 180° [18].

Under the normal conditions, hydrogen peroxide exists in the liquid form. Due to the asymmetry of H_2O_2 molecule and its high polarity ($\mu = 0.7 \cdot 10^{-29}$ coulomb \cdot m = 2.1 Debye).

Although H_2O_2 molecule can be decomposed, there are very few examples where the activation energy of the decay is actually identified with the dissociation energy of the O-O - bond. In the presence of transition metals, it is usually 42-50 kJ/mol instead of 126 kJ/mol expected for thermal decay. It was shown [19] that intermediate reactions in the process of hydrogen peroxide decomposition are expedient from the energetic point of view with transition species HO^\bullet and HO_2^\bullet [20].

A stepwise mechanism of oxygen production in Fenton reaction was revealed in [21]. It was shown that the cleavage of O-O bond in the coordinated H_2O_2 molecule does not provoke the immediate appearance of HO^\bullet radical; instead is formed active intermediate $[\text{Fe}^{\text{IV}}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$ with two linked OH-s, with activation barrier less than 60 kJ/mol.

3. Electron Transfer Reactions with the Involvement of Hydrogen Peroxide

Hydrogen peroxide is the simplest peroxide - a compound with an oxygen-oxygen single bond, and can act as either oxidant or reducer:

oxidant: $\text{Me}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Me}(\text{H}_2\text{O}_2)^+ \rightarrow \text{Me}^{2+} + \text{OH}^\bullet + \text{OH}^-$

reducer: $\text{Me}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Me}(\text{HO}_2)^+ + \text{H}^+ \rightarrow \text{Me}^+ + \text{HO}_2^\bullet$.

One of the most often oxidative reactions in the environment includes H_2O_2 participation in the series of consecutive transformations, according to the general scheme (Figure 1) [22]:

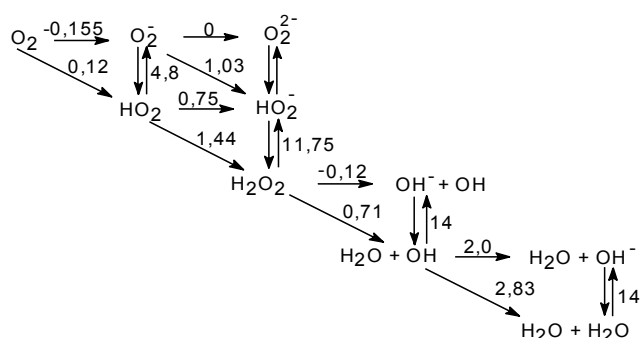


Figure 1. Transformations of O_2 to H_2O_2 and then to H_2O . Numbers near the inclined and horizontal arrows means decrement of redox-potential in volts. Numbers to the right of vertical arrows are the values of pKa for corresponding acid-base equilibria.

Four-electron transfer only occurs in certain biologic systems, whereas the more often is the two- or one-electron transfer, giving intermediate products of O_2 reduction.

From the energetic point of view, the two-electron transfer to the O_2 and further H_2O_2 reduction is profitable, because the main energy release occurs during the transfer of the second electron. Single electron transfer with the free radicals formation is energetically less preferable in comparison with synchronous reaction, provoking the formation of even-electron stable molecules.

3.1. Metal Complexes with Hydrogen Peroxide

Since the 1970's, the role of transition metal complexes (Mn, Fe, Cu) in the activation of oxygen and hydrogen peroxide have been studied by Moldovan researchers, who have elaborated the theory of partial charge transfer complexes (PCTC) [23], see Figure 2.

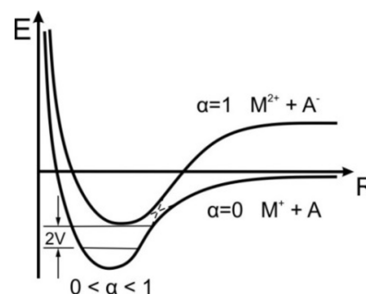


Figure 2. Energy curve of partial charge transfer complex. The width of the energy gap between the main and excited terms in charge transfer complexes is about 2 volts. The transition from the initial state to the final one occurs not in the minimum of the potential pit but in the intersection zone of the terms.

Thermodynamic equilibrium is established between the primary complex and complex in the excited state, with the partial transfer of one or two electrons from donor to acceptor. Due to this phenomenon, PCTC can manifest the properties of both the initial chemicals, and final products, thus demonstrating the specific reactivity.

Figure 3 demonstrates a general set of hydrogen peroxide reactions with participation of PCTC.

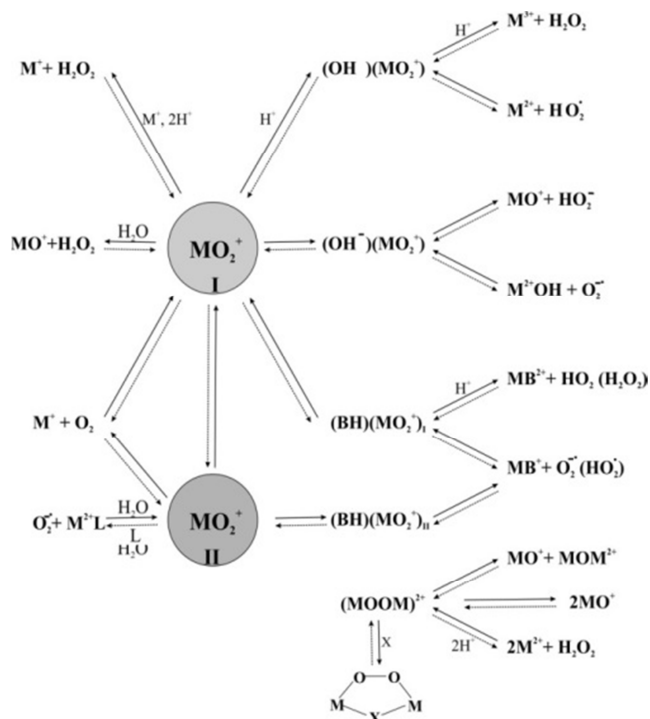


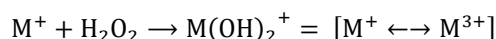
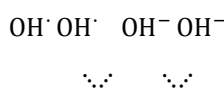
Figure 3. A set of reactions with charge transfer metal complexes as catalysts. PCTC is pure quantum phenomenon with structures superposition with full charge transfer (lower site II, where the central metal ion can be regarded as oxidized) and without charge transfer, where the central ion behaves as a reduced one (upper site I).

In case of PCTC the products of one-electron transfer (free radicals) not necessarily leave the complex, what is important for realization of some selective processes, for instance, in natural waters, in wines, in juices etc. and determines their quality.

Our detailed studies of a series of PCTC made it possible to estimate and demonstrate the viability of the proposed theory, in its applications to homogeneous catalysis, waste water treatment, wine production, development of chemical-biologic processes in human body, etc. [24-26].

3.2. Two-electron Inner-sphere Transfer

In case of two-electron inner-sphere transfer, an intermediate complex is formed in which metal ion or atomic oxygen have the maximum oxidation state:



In acid environment, MO^+ and $\text{M}(\text{OH})_2^+$ interact with H^+ forming the reactive particles: $\text{MOH}^{2+} \equiv (\text{M}^{2+} \dots \text{OH} \leftrightarrow \text{M}^{3+} \text{OH})$ complex and metal ion in the highest oxidation state M^{3+} . In the neutral environment, MO^+ and $\text{M}(\text{OH})_2^+$ particles are hydrolyzed with the formation of hydroxo-derivatives. The hydrolysis can be accompanied with water oxidation to OH radical.

An aqua oxoiron (IV) species are believed to play an important roles in environmental and catalytic chemistry, and have been proposed by some researchers as alternatives to HO-radical in the composition of Fenton oxidizing reagent, that is an intermediate produced in the reaction between Fe^{2+} aq and H_2O_2 in aqueous solution. The ferryl intermediate, most probably $[(\text{H}_2\text{O})_5\text{FeIV}=\text{O}]^{2+}$, has not been detected in the acidic and neutral solutions. Such a complex, however, is believed to be generated in the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ /ozone reaction, which simultaneously yields an O_2 equivalent, therefore, the intermediate can be described as an ozonide complex. The ozone-generated transient species decays exponentially in acidic aqueous solution, bears a 2+ charge, oxidizing the organic and inorganic substrates. All these findings confirm that formula of complex is: $[(\text{H}_2\text{O})_5\text{Fe}(\text{IV})=\text{O}]^{2+}$. The decisive spectroscopic data of this species are described in [27].

4. Applications of Hydrogen Peroxide

Hydrogen peroxide is a promising ecologically pure oxidant. Thus, advanced oxidation with hydrogen peroxide comprises a range of chemical processes aimed at tackling pollution in water, air and soil [28, 29]. Using H_2O_2 as an oxidant in technological processes is beneficial, instead of the conventional strong oxidants currently used in pollution protection. H_2O_2 as an environment-friendly oxidant.

It also may be used in the photoinitiated reactions of toxic organic pollutants decomposition in water environments,

along with the application of, Fenton system, photoinductors, microbial systems [30].

At the same time, hydrogen peroxide has numerous biopharmaceutical applications. Its usage in medicine has started in the early 1800's, due to the anti-microbial effects and now it is broadly used either alone or in combination with other agents, improving their characteristics [31-33].

One more example of drug with great therapeutic efficacy is Enoxil produced from the winery wastes by oxidation with hydrogen peroxide [34-36].

Another interesting application area of hydrogen peroxide is agriculture, in composition of a plant growth stimulator such as *Cerera* agent [37]. Before seeding and during the vegetation period the seeds treated with water solution containing Cu ions and $10^{-6} - 10^{-4}$ M H_2O_2 have demonstrated higher sprouting capacity. The best effect was observed for tomato, lettuce, onion, and soya. The first sprouts appeared 5-7 days earlier, and productivity was 132% higher as compared to control crops [38].

5. Photo-processes with Hydrogen Peroxide Involvement

There is an extensive literature on photo-processes occurring in natural waters and their application in waters and wastes treatment technologies. Since 1980's, the numerous studies have provided considerable insight into the range of light-driven processes that occur in the natural aquatic environment or result in degradation of toxic or troublesome substances in waters and wastes. In addition, the detailed laboratory studies in simple, well defined systems have provided information on possible kinetics and mechanism of photo-processes in the complex natural waters and wastes [39].

In many cases the natural photodegradation of pollutants can be even more important than their industrial treatment. The rates of the photochemical processes near the surface are dependent on several environmental factors such as season, latitude, time-of-day, depth of the water body [40].

Very peculiar study of herbicides photolysis in natural and mineral waters was reported by Benitez, 2004 [41]. In this work the photooxidation of the selected herbicides in some natural and mineral waters was carried out to analyze the influence of water quality parameters and to propose a general kinetic model for herbicides elimination from the natural waters, using the kinetic parameters and quantum yields.

Photogeneration of free radicals (sometimes via singlet oxygen formation) can occur with participation of the dissolved organic matter, as shown by Sandvik et al., 2000 [42], as well as heterogeneous suspensions of photo sensitive nano-particles, such as TiO_2 , demonstrated by Salvador, 2007 [43].

It is still a hypothesis whether the photogenerated free holes in the valence band are trapped by the adsorbed water species to produce adsorbed OH radicals, or by the terminal oxygen ions. Nevertheless, the authors of this chapter agree with Salvador's point of view. OH radicals in the water layers

nearby the TiO_2 surface cannot be photogenerated, moreover, the adsorbed OH radicals may not be desorbed and diffused into the aqueous solution. Such mechanism can be most probable, because we only see the pollutants degradation, but not the photoinduced water oxidation. The sources and sinks of hydroxyl radicals upon irradiation of natural water solutions are in detail discussed by Vion et al, 2006 [44].

It is to be noted, that in some publications the proper conditions for water treatment with hydrogen peroxide and/or photoinitiated catalytic processes are not shown. For instance, in the paper of Horvat and Huszank (2003) [45] the concentration and pH values differ by four-five orders from what can be expected in natural waters, so it is difficult to extrapolate these results to environment.

The use of humic acids, well known sensitizers of photocatalytic processes, able to promote the contaminants degradation in natural waters, in photochemical treatment has been discussed in [46]. Surprisingly, it was found that humic acids binding to magnetite nanoparticles Fe_3O_4 have resulted in lower yields of reactive oxygen species (ROS) generation. The data also indicate that ROS production of both free and bound humic acids depends on the nature of particular humic acid.

Marchisio et al. in 2015 [47] studied the photogeneration of reactive transient species under the irradiation of natural water samples. It was found, that chromophoric dissolved organic matter (CDOM) in surface waters is a photochemical source of several transient species such as CDOM triplet excited states ($^3\text{CDOM}^*$), singlet oxygen ($^1\text{O}_2$) and the hydroxyl radical OH. By irradiation of lake water samples, it was shown that the quantum yields for the formation of active transients by CDOM vary depending on the irradiation wavelength range, in the order $\text{UVB} > \text{UVA} > \text{blue}$.

In case of excessive intensification of free-radical processes and an increased contents in manganese ions in water, a super-oxidative state of the natural aquatic environment that is toxic for aquatic biota can be formed. The carriers of super-oxidative equivalents are microcolloidal manganese particles in the mixed-valence state of Mn (III, IV) formed by the interaction of OH radicals with Mn^{2+} ions, as shown by Baral et al., 1986 [48]. In composition of these nanodimensional, metastable particles, Mn (III) ion is surrounded by Mn (IV) ions. This is a kind of "repository" of OH-radicals within the micro-colloidal Mn (III, IV) particles.

Of course, OH radicals are not the unique active species, which can be readily photogenerated. Wu et al., 2015 [49] studied the persulfate activation induced by Fe (III)-ethylenediamine-N, N'-disuccinic acid under the dark and irradiation conditions and the reactivity of generated sulfate radical under the wide range of experimental conditions, by experimental kinetic studies and modeling.

6. Hydrogen Peroxide in Natural Water

6.1. Contents in Hydrogen Peroxide in Environmental Compartments

Hydrogen peroxide can be found in atmosphere, surface

and ground water, it is a natural component of any water reservoir; its contents in wet precipitates varies from 10^{-6} to 10^{-4}M , and in nonpolluted water bodies within the range 10^{-7} – 10^{-6} M. The higher is environmental pollution, the lower is H_2O_2 contents [50].

According to V. Sinelnikov [51], H_2O_2 contents in unpolluted Volga river water is around 10^{-6} M; its daily concentration being determined by solar illumination, affecting its both photochemical and biological generation, increased in the daytime and decreased at night.

In seawater the amount of hydrogen peroxide is lower, as compared to the fresh waters [52]. After the rain, H_2O_2 contents on the ocean surface sharply increases (by 10-100 times), but in several hours returns to the stationery level [53].

6.2. Natural Water Quality: Impact of H_2O_2 Formation and Decomposition

The natural water quality depends in a large degree on hydrogen peroxide concentration [54]. The specifics of natural water bodies is relatively low concentrations of transition metals, but in the presence of living species, the reducing equivalents are formed as a result of metabolism. These equivalents are readily oxidized with hydrogen peroxide (peroxidase type reactions).

Hydrogen peroxide is formed in natural systems through the following ways:

1. Washing out from atmosphere;
2. Photochemical action on dissolved organic substances (DOS) and transition metal complexes;
3. Catalytic processes of DOS oxidation by dioxygen;
4. Released during the living activity of bacteria and algae;

Hydrogen peroxide decomposition can occur due to the biotic or abiotic factors, including reactions of first and zero order with regard to $[\text{H}_2\text{O}_2]$. The rate of biotic degradation is usually proportional to biomass amount. The overall equation is:

$$W_d = W_r + W_b + k [\text{H}_2\text{O}_2], \text{ where:}$$

W_r – formation rate of the peroxidase type reducing substances;

W_b – biotic degradation rate;

k – effective 1st order rate constant.

Under the quasi-stationary conditions the W_d is equal to W_r , the quasi-stationary concentration being:

$$[\text{H}_2\text{O}_2] = (W_r - W_b)/k.$$

6.3. Redox State of Natural Waters and Water Quality Indicators

Our studies [55] have revealed that generally natural waters exist in one of two redox states, depending on the ratio of H_2O_2 and reducing agents concentrations [56]. In the oxidative state biologically necessary amounts of hydrogen peroxide (10^{-6} - 10^{-5} M) have been registered in water. The quasi-reducing state is characterized by the absence of H_2O_2 traces in water, whereas the presence of reducing equivalents (phenols, dienols, sulfur compounds) can be determined by titration with H_2O_2 , consumed in peroxidase-type reaction.

The superoxidized state occurs very seldom, when along with hydrogen peroxide, some other oxidizing substances are detected, specifically, half-products of technological cycles, including active chlorine, Cr (VI) and KMnO_4 .

Appearance and duration of the unstable water redox states can differ in different seasons (Figure 4). It was observed, that the changes in water redox state are accompanied with the important changes in quality of living environment. At the

same time, the standard hydrochemical indicators (pH, Eh, O_2 , TOC, DOC, BOD, etc.) show no essential changes. This condition usually occurs in the water bodies during the blossoming starting of blue-green algae, prior to their mass development, under the temperature 18-20°C, at the windless weather. Hydrogen peroxide generated in photochemical processes in quasi-reducing state is completely consumed for the „titration” of the reducing equivalents.

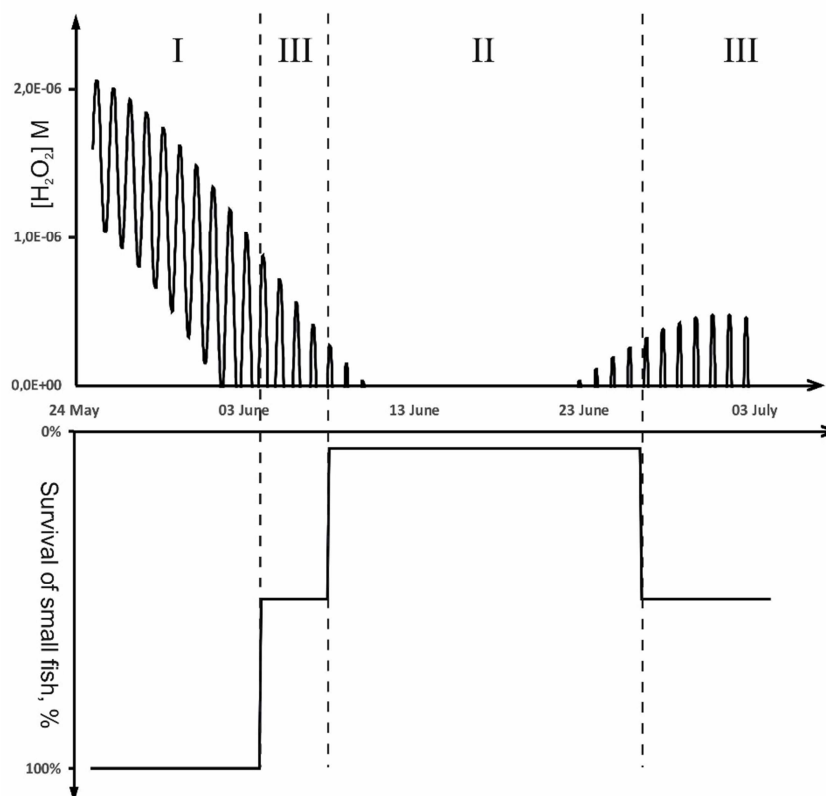


Figure 4. Seasonal redox state of Volga river waters: I – oxidized state; II- quasi-reducing state; III - unstable state.

The evolution made it natural that the living organisms can only exist in oxidative conditions and die in the reducing environment. For example, daphnia, infusorians, juvenile fish die shortly if hydrogen peroxide is absent, even if the dissolved oxygen amount is close to its normal limit. Another impact of reducing conditions is the burst of pathogenic microflora, which releases toxins, affecting even the people [57–58]. In the work [59] it was demonstrated that H_2O_2 also functions as a signaling molecule, controlling the different essential processes in plants and mammals.

By biotests methods we have found that the treatment of municipal waste water or pulp & paper mills sewage with small additives of H_2O_2 comparable to the contents in reductive substances in water, leads to their detoxification [60]. The similar effect of detoxication with hydrogen peroxide was also observed when the fish liver in the area of wastewater discharges was studied, and the increase in monooxygenase activity was detected. It was found that the water-soluble reduced sulfur compounds are reducing substances interacting effectively with H_2O_2 and inert with regard to O_2 [61].

We hope that this brief review explains the new wave of hype to HY (drogen) PE (roxide). Hyper interest to this unusual substance is rising.

7. Conclusions

1. Hydrogen peroxide is a natural product that inevitably appears during the redox reactions with the involvement of molecular oxygen.
2. “Peroxidase” processes play the most significant role in the natural waters self-purification and their quality formation. Hydrogen peroxide is also widely used in the industrial waste water purification systems and water treatment technologies.
3. Thermal activation of hydrogen peroxide molecule is improbable – for this process to be realized the transition metal ions as catalysts are needed. Photoinitiation of radical processes with hydrogen peroxide oxidation is also important.
4. Hydrogen peroxide is an essential component of aquatic ecosystems, without which the survival of certain

vertebrates and their larvae becomes impossible, even in conditions of the dissolved oxygen excess. This can be apparently attributed to the fact that during the evolution, hydrogen peroxide in water has emerged prior to the appearance of oxygen atmosphere.

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