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New Aspects of the Role of Organisms and Detritus in the Detoxification System of the Biosphere

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Abstract—The review covers new aspects of the participation of organisms in the detoxification system of the biosphere. Problems of detoxification of toxic environmental pollutants are analyzed. New author's experimental data in combination with a large amount of information in the scientific literature gave rise to a new concept of the role of biogenic detritus and related nutrients in environmental detoxification (ex-living matter concept). This may be useful for the development of new technologies for remediation and decontamination of the environment.

Keywords: biosphere, detoxification, pollution control, toxic chemical elements, immobilization, sorption, biogenic detritus, ex-living matter

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INTRODUCTION

Study of the problem of detoxification of harmful substances in the biosphere is closely related to several areas of environmental chemistry. Many authors studied problems of migration and cycling of chemical elements in the biosphere [1–3], elemental composition of environmental objects [2–22] and other aspects of biosphere chemistry [18–49], and the role of organisms in the formation of certain chemical parameters of the habitat [5–7, 15–17, 50–79]. Studies of the chemical–biotic interactions [11, 12, 14–22, 25–47, 55, 67, 72–75, 78–80] and accumulation of a large amount of information on the geochemical environment (see, e.g., [14–17, 21, 23, 47, 55, 73, 75, 80]) have revealed some unresolved issues, which leads to the need to re-examine the question of how organisms are involved in the transformation and detoxification of habitats.

It is interesting to analyze how toxic chemical elements are neutralized in the biosphere during natural ecological and biogeochemical processes. New important relevant data are actively accumulating in experimental studies conducted in the laboratory of biogeochemistry of the environment of the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences [15, 16], as well as in many laboratories of the world [81, 82].

V.I. Vernadsky emphasized the importance of studying migration of chemical elements in the biosphere and relations between the activity of living matter and the physicochemical characteristics of the biosphere [5–7, 74], as well as the importance of various ways of the influence of living matter on the environment. Data on the chemistry of the biosphere [3, 4, 15–17], geochemical environment, and factors affecting the concentrations of chemical chemical elements [3, 4, 15–22, 25–47, 55, 67, 72–74], migration of elements and biogeochemical flows in the biosphere [67, 22, 28, 30], and self-purification of the environment from chemical pollutants [28, 63–69] rapidly accumulate. The new data require additional analysis, so that it is necessary to formulate appropriate generalizations.

The objective of this analysis is to consider the role of organisms and substances derived therefrom (biogenic detritus and other detritus-like substances) in the detoxification system of the biosphere with account taken of our data.

It is necessary to distinguish two aspects of the problem under study:

(1) The role of living organisms during their vital activity;

(2) The role of biogenic detritus and related substances of biological origin which were referred to

as ex-living matter (ELM) in our previous publications [29, 32, 78, 79].

Role of living organisms in the detoxification of the environment during the period of their vital activity. The useful role of living organisms in detoxification of the environment can be traced through the example of aquatic ecosystems. In our previous publications, a comprehensive mechanism of water purification in freshwater and marine ecosystems has been discovered and detailed to some extent [28, 63–65, 67–69]. In these studies, attention was paid to the multifunctional role of biota and the entire biological community [63, 64]. A significant but sometimes not obvious contribution of organisms to non-biological (physical and chemical) water purification factors was revealed [28, 64]. As a result, a theory of biotic self-purification of water was created [28, 63, 64]. Studies of this series were supported and cited by other researchers [12, 14].

Thus, the useful function of ecosystems and biological community in the performance of ecosystem services in maintenance and improvement of water quality, assimilation and purification of anthropogenically contaminated and waste water, and environmental safety (environmental safety) of water supply sources was analyzed more deeply than before. These studies have proven even higher utility of many species of aquatic ecosystems, which supports the arguments for the protection of wildlife and biodiversity.

It is necessary to consider in more detail the role of biogenic substances in the detoxification of the environment.

Role of biogenic detritus and related substances of biological origin. The role of biogenic detritus and related substances of biological origin (ex-living matter, ELM) [29, 32] in the detoxification of the environment is increasingly understood.

As noted in [78], substances related to ELM makes a significant contribution to the immobilization of a number of chemical elements, decrease in their bioavailability, and partial inhibition or interruption of their circulation in the geochemical environment. The emphasis given to the important role of substances of this type provides another vivid example of what V.I. Vernadsky wrote about: “During the geological time, *the power of living matter in the biosphere grows*, and its significance for the biosphere and its effect on the inert matter increase” (italics of V.I. Vernadsky) [6].

Taking into account the phenomenon of immobilization of toxic elements, the author believes it necessary to pay attention to the following fact. In some cases, living matter, creating favorable conditions for itself, affects inert (non-alive) and sometimes toxic substance of the environment not directly but indirectly. The mediator is a substance that we proposed to call a substance of the third type or former living matter (ex-living matter, ELM) [29, 32, 78, 79]. It immobilizes toxic elements. Examples of experimentally observed immobilization of toxic elements are given below.

The following components of the biosphere can be regarded as ELM (some of the classes listed below may intersect and overlap one another):

(a) organic matter of pellets excreted by soil and aquatic invertebrates, including benthic invertebrates (e.g., mollusks) and zooplankton;

(b) substance of dead organisms;

(c) plant mortmass, including leaf litter, fallen pine needles, branches, and other components;

(d) biogenic detritus (particulate organic carbon, POC) in aquatic ecosystems (total content in the biosphere about 3×10^{16} g of carbon [73]);

(e) dissolved organic matter (DOC, dissolved organic carbon) in freshwater and marine ecosystems (total content in the biosphere about 1×10^{18} g of carbon [73]). This class of substances also includes exometabolites and organic ligands;

(e) humus (both soil and water);

(g) biogenic inorganic particles, e.g., shells of some aquatic microscopic organisms, including diatom algae, radiolarians, foraminifera, and coccolithophorids. The specific surface of these natural sorbents is 5–120 m^2 per gram [23];

(h) organic matter of bottom sediments of the World Ocean and continental water bodies (estimated at 10^{22} g of carbon) [73];

(i) various exometabolites and biopolymers released by organisms to the environment, as well as products of their biochemical and chemical transformations (products of microbiological processing, oxidation with oxygen, photoreactions, including photodegradation, etc.).

As additional examples, we note that such terms as forest litter, dead organic matter, phytodetritus, dead of

Table 1. Microcosm composition

Component	Microcosm no. 1 (control)	Microcosm no. 2 (experiment)
Mollusks *Unio pictorum*, number of individuals	6	6
Mollusks *Viviparus viviparus*, total biomass, g (wet)	33.7	31.6
Macrophytes *Ceratophyllum demersum*, g (wet)	16.3	15.1
Water (settled tap water), L	5	5

Table 2. Composition of M7 solution and amounts of metal salts added to microcosms

Metal salt	Amount of salt in M7 (1 L), mg	Amount of salt added to microcosm (1 mL of M7), μg
$Fe_2(SO_4)_3 \cdot 9H_2O$	40	40
$K_2Cr_2O_7$	40	40
$Cd(CH_3COO)_2 \cdot 2H_2O$	20	20
$MnSO_4 \cdot 5H_2O$	40	40
$CuSO_4 \cdot 5H_2O$	40	40
$ZnSO_4$	40	40
$CoSO_4 \cdot 7H_2O$	40	40

organic matter, and others are used for terrestrial ecosystems [1, 2, 10, 52]. Analysis of published data on humic substances is given in [24].

The total amount of ELM is very large and is several orders of magnitude higher than the total amount of living matter in the biosphere.

An example of the formation of appreciable amounts of the third type of matter is the accumulation of biogenic detritus on the bottom of aquatic systems with organisms. For brevity, substances of the third type will be denoted ELM (ex-living matter) [29]. This report focuses on such constituent of ELM as biogenic detritus. However, it should be emphasized that it is by no means the only representative of the third type of matter.

It is important that in many cases the actually observed substance of the third type, for example, in aquatic ecosystems, is not simply the lifeless bodies of earlier living organisms. After their death, microorganisms take effect, and chemical reactions such as oxidation, degradation, etc. are initiated. After a short time, the observed substance is the product of many modifications and transformations. In addition, molecules of polymers (e.g., polysaccharides) and other substances excreted during the lifetime play an important role. Obviously, the actually observed matter of the third type is complex and is the result of many processes.

EXPERIMENTAL

Experimental studies revealed additional data on the possibility of binding of a number of chemical elements, including toxic ones, to biogenic detritus. The results of prolonged incubation of microcosms with macrophytes showed the following (Tables 1–3).

Experiments with microcosms and solutions of metals. The experiments [29, 32, 34, 41] are described in Tables 1–3 which contain (1) the compositions of the examined microcosms (Table 1), (2) amounts of metal salts added to the microcosms (Table 2), and (3) elemental composition of biogenic detritus in these experimental aquatic ecosystems after incubation (Table 3).

The composition of the M7 solution added to the microcosms is given in Table. 2. The total volume of M7 added over a period of 5 weeks was 10 mL or 2 mL per liter of water in the microcosm (5 L).

Binding of a group of elements, including metals and rare earth elements, as well as toxic nanoparticles, to biogenic material. Along with other elements, As, Be, Cd, Co, Cr, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, V, Zn, Bi, Ga, Gd, Ge, Ho, Ir, Nb, Rb, Ta, Tb, Te, Th, and Tm were studied. The data on binding of copper-containing nanoparticles to biogenic material were obtained in cooperation with J. Tyson, M. Johnson, and B. Xing (University of Massachusetts, US) [56–58]. Binding of nanoparticles to biomass and mortmass of a number of plant species, including *Myriophyllum aquaticum*, *Ludwigia* sp., *Typha* sp., and *Gingko biloba*, was studied. It was found that copper oxide and titanium oxide nanoparticles were immobilized by binding to the above biogenic materials.

Table 3.

Chemical element[a]	Microcosm no. 1 (control)	Microcosm no. 2 (experiment)	Experiment-to-control ratio, %	Comment
As	1.85	1.42	76.8	No excess
Co (+)	0.67	9.36	1397.0	Excess
Cd (+)	0.62	2.25	362.9	Excess
Pb	11.75	12.25	104.3	No excess
Cr (+)	0.32	56.00	17500.0	Excess
Fe (+)	4830.00	5788.00	119.8	Slight excess
Mn (+)	3233.00	4729.00	146.3	Excess
Zn (+)	1398.00	2501.00	178.9	Excess
Cu (+)	293.00	592.00	202.0	Excess

[a] The elements marked with a "plus" sign were added to the aqueous medium of the microcosm.

These results are consistent with our NMR data which showed effective binding of zinc-containing nanoparticles to some amino acids (tryptophan) [48]). Additional data on the binding of nanoparticles of different nature, including those containing toxic elements, to biogenic matter are given in [70].

Experiments with other types of biogenic material and copper. Recently, the author conducted new experiments with some other types of biogenic material. New data were obtained on the immobilization of copper and other heavy metals. The relevant publications are now in preparation.

Humus substances in soils and waters. There are extensive published data on the binding of many toxic compounds to humic substances [76, 77]. The binding of copper and lead to soil humus was characterized using X-ray absorption spectroscopy [76]. Similar X-ray absorption spectroscopy studies were carried out by other authors [8, 9].

Analysis of vast new information obtained by studying speciation of heavy metals and metalloids in soils by synchrotron X-ray technologies of the third generation [8, 9] led to the following conclusions. The chemical affinity of heavy metals and metalloids for specific soil components has been characterized. A number of heavy metals, specifically those that are most often referred to as dangerous ecotoxicants, fall into the category of organophiles, i.e., elements exhibiting chemical affinity for the organic matter of soils [8]. Organophiles are zinc, lead, copper, cadmium, and mercury. The first four elements of this list (Zn, Pb, Cu, Cd) also behave as manganophiles. Mercury is a chalcophile [8]. This indicates a variety of chemical factors that affect the behavior and immobilization of toxic chemical elements in soils. The overall pattern is complex and in no way should it be simplified. Essentially, the organic matter of soils makes an indisputable significant contribution to the immobilization of a number of these elements.

Binding of toxic elements by bottom sediments. Studies performed in many laboratories has revealed that many toxic substances accumulate in bottom sediments and that the concentration of organic matter therein is important here. These findings are closely connected with the above examples. Analogous results were obtained for binding of Cd, Fe, Co, Ni, As, Cr, Pb, Cu, and V by bottom sediments of the Ivankovo Reservoir (upper reach of the Volga River, Tver oblast, Moscow oblast) [22]. Organic matter of bottom sediments is biogenic in nature and, of course, it may be regarded as ELM.

There are additional data on the binding of chemical elements, including toxic metals, to biogenic materials. Such data have been obtained in many laboratories. For example, effective binding of Al(III), Cu(II), and Ag(I) to ten biologically generated materials immobilized on a polysilicate matrix was demonstrated. The examined biogenic materials included sphagnum peat, topsoil, several other peats, dead biomass of *Chlorella vulgaris*, and cellular material of *Datura innoxia* [72].

The great functional significance of biogenic material in natural ecosystems is clearly manifested in the case of freshwater and marine ecosystems. The biogenic organic matter constituting bottom sediments contributes significantly to pollutant binding to bottom sediments, which is one of the processes of self-purification of water in aquatic ecosystems [28, 63, 64, 67–69].

An additional array of data on biogenic organic material in ecosystems, especially in aquatic ones, has been reported in many other publications, including [73, 75].

These examples illustrate the diversity of experimental data which allowed substantiation of our conclusion on the essential role of ELM in detoxification of the environment.

It should be emphasized that effective heavy metal binding to ELM (e.g., biogenic detritus) indicates important functions of ELM for the biosphere, namely detoxification, conditioning, purification, and stabilization of habitats for living organisms. These functions are important and necessary to maintain favorable environment for living organisms. Examples supporting these ELM functions have been reported by many authors.

Practical utility of the author's ideas about the role of detritus and ex-living matter in the biosphere and its detoxification system. The above stated indicates significant role of ELM in the binding of toxic elements and their detoxification. This should be taken into account when carrying out environmental monitoring. The latter should include analysis of the concentrations of toxic elements in those components of the environment that contain ELM, specifically biogenic detritus of bottom sediments and humus in terrestrial ecosystems.

This proposal introduces a new emphasis and supplements the existing monitoring system. The existing monitoring system includes measurement of concentration of chemical elements in bottom sediments. However, this is insufficient since biogenic detritus constitutes a variable part of bottom sediments.

Certainly, toxic elements also bind to other components of bottom sediments of aquatic ecosystems, such as clay and iron and manganese hydroxides [22]. To evaluate the heavy metal content of these components or complexes with them, certain metal extraction methods are used. However, the question is so important that further studies are required. It is necessary to verify the selectivity and specificity of these extraction methods, as well as their reliability as applied to bottom sediments.

The above theoretical concepts introduce a new element in the analysis of empirical data on the concentrations of chemical elements in bottom sediments of aquatic ecosystems. The concentration level of some toxic elements in this component of the biosphere is much higher than the background level, which is caused by human activity. Examples of such high values in sediments of some rivers of Moscow oblast of the Russian Federation are given in [54].

The quantitative characteristics indicating excess lead and silver concentrations in bottom sediments, given in [54], can be compared with the corresponding data for water. The concentration of lead in water of the Pakhra River exceeded the background value by a factor of ~8, whereas the maximum excess for anthropogenic silt was significantly higher, 30 times. In the same river, the maximum silver content of water was 4 times higher than the background concentration. Excess silver in anthropogenic silt was estimated at a value two orders of magnitude higher, 300 or more. In further studies it is advisable to take into account organic matter content of bottom sediments.

In aquatic ecosystems, a significant amount of ELM is present in the forms of suspended organic matter (SOM) and dissolved organic matter (DOM). As follows from the aforesaid, it is necessary to conduct a more complete monitoring of the concentrations of toxic metals bound to SOM and DOM. This will also require methodological improvements.

The above theoretical propositions can be used in analyzing concentrations of chemical elements in soils. In some cases, heavy metal content of soils significantly exceeds not only background values but also the maximum allowable concentrations. An example is provided by the concentrations of heavy metals in soils in urbanized or industrial areas [8, 9, 45, 46], including Semipalatinsk [46] and other territories in various countries.

When analyzing metal concentrations in soils and bottom sediments, it is advisable to take into account the organic matter content of soils and sediments as a factor that favors immobilization of pollutants such as heavy metals.

Apparently, in the future it will be necessary to carry out additional monitoring of the concentrations of toxic metals not only in soils in total but also in the most important component of the soil, soil humus. Probably, it will also be necessary to improve methods for such monitoring.

It was found that Pb, Cu, Co, Ni, and Zn form so-called inner-sphere complexes with organic compounds in soils [9, 60, 76, 77]. EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy is an efficient tool for studying metal binding to organic matter in soils. E.g., according to the EXAFS data, organic substances play an important role in the immobilization of lead in soil [61].

Likewise, when comparing data on the content of heavy metals and other toxic elements in the bottom sediments of aquatic ecosystems, it will also be advisable to take into account information on the organic matter content of these sediments. In this part of aquatic ecosystems, the organic matter is mainly either biogenic detritus or its transformation products.

Thus, the material of this study makes it necessary to propose new steps in improving the ecological monitoring of both terrestrial and aquatic ecosystems.

In general, the above data emphasize the advisability of increasing attention to the functional role in the biosphere of various forms of organic matter that are not part of the biomass. This may be useful for practical issues of assessing the state of ecosystems and environmental monitoring.

CONCLUSIONS

A significant part of the organic matter not included in the biomass is detritus; the considered types of matter include dissolved organic matter (DOM), dissolved organic carbon (DOC), suspended organic matter (SOM), particulate organic matter (POM), plant mortmass, and other types of organic matter. Taking into account that these types of organic matter perform some common functions important for the biosphere, it seems reasonable to combine them under a common name. The experimental results and analysis of scientific literature lead to the following conclusions:

(1) Biogenic detritus and related substances (ex-living matter, ELM) [29] performs important ecological and biogeochemical functions, including conditioning of geochemical environment, e.g., binding of certain chemicals and chemical elements (including toxic ones). This can reduce the concentration of these toxic components in the environment, specifically in the aquatic environment, which is beneficial for the habitat of living organisms.

(2) The results of recent studies confirm the earlier prediction [78] that new data will be obtained on the great role of ELM in the environment, functioning of the biosphere, and decontamination or conditioning of environmental components, including the aquatic environment.

(3) The role of ELM in environmental impact assessment and environmental monitoring needs to be taken into account more fully.

(4) The above-mentioned studies of the immobilization of toxic chemical elements by biogenic detritus contribute to the analysis of fundamental concepts and systematization of extensive empirical data on the geochemical environment and the biosphere [12–15, 17–19, 27, 31, 35, 37, 38–42], which is useful for understanding the natural processes of neutralizing toxic elements. On this basis, additional opportunities appear for the development of new ecotechnologies for the purification and neutralization of industrial wastes and sewage [3, 21, 22] and other fields of activity. The author predicts that these technologies will be based on the sorption of toxic substances by biogenic materials.

In general, the studies performed showed that the role of biogenic detritus and other forms of biogenic organic matter not included in the biomass (ex-living matter) is more important and fundamental than believed previously. In fact, this matter interferes very significantly with migration of chemical elements and immobilization of toxic substances. As a result, the availability of these substances for living organisms is reduced, and detoxification of the habitat is achieved to some extent.

This publication is based on the author's previous publications [32, 78, 79, etc.], in particular on the review written for the collection of papers [80].

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