

Freshwater Plankton as Sorbent: Differences in the Sorption Properties of Live and Dead Plankton

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Abstract—The distribution coefficients of a number of chemical elements between live and dead plankton and aquatic medium were determined experimentally. The sorption isotherms of macro- (Mg, Ca) and microelements (Sr, Ba, Mn, Fe, REE, Th, U) on plankton as biosorbent under the conditions when their level exceeds the natural background in water follow the Langmuir equation. The equation parameters for samples of live and dead plankton differ statistically significantly. In the sorption affinity level ($\log K_d$ [mL g⁻¹] ~3–5), freshwater plankton can be considered as effective biosorbent. Electron microscopic examination with local multielement analysis revealed abnormally high content of manganese in the form of adsorption colloid for *Trachelomonas acanthostoma* var. *acanthostoma* plankton alga in separate water samples taken from the cooling pond of the Beloyarsk NPP.

Keywords: plankton, sorption, cooling pond of Beloyarsk NPP

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Operation of nuclear power plants and of other enterprises of nuclear fuel cycle requires permanent improvement of environment protection technologies in connection with the use of water from cooling ponds for industrial purposes and with inevitable generation of liquid radioactive waste [1]. In the zone under impact of such enterprises, water bodies are subjected to the action of various manmade pollutants owing to the supply of chemical substances, including heavy metals and low-level solutions, which are taken up by hydrobionts and bottom sediments owing to specific features of aquatic ecosystems. As a result, the content of these pollutants in water appreciably decreases [2–5]. The possibilities of using hydrobionts, in particular, of zoo- and phytoplankton, as biological sorbents (biosorbents) for preventing the environment pollution with manmade pollutants, including radionuclides, are still poorly understood. Hydrobionts are today practically the only large-scale means for removing manmade radionuclides from natural aquatic medium without making a special production cycle and without exerting harmful effect on the ecosystem. For example, it

has been demonstrated by the example of the Beloyarsk Reservoir that the radionuclide accumulation factors for plankton are higher by several orders of magnitude than those for other hydrobionts. Thus, plankton ensures the most complete binding and removal of radioactive elements from water [2]. The scales of sorption processes involving hydrobionts demonstrate the need for a more detailed study of properties of freshwater plankton as biosorbent of collective action, capable to resist to emergency discharges. This is a topical physicochemical and radiochemical problem.

The main quantitative characteristic of the biosorbent is the distribution coefficient (K_d) [6] or accumulation factor (AF) [7]. K_d can be used for adequate comparison of the sorption properties of plankton on the basis of the formalism of the adsorption theory, as demonstrated by the example of the sorption behavior of the Pb(II), Cu(II), Ni(II), Cd(II), and Zn(II) ions [8–16]. Plankton as biosorbent, in contrast to sorption materials, can exhibit sorption activity both individually and in combination with inorganic colloids [17]. The

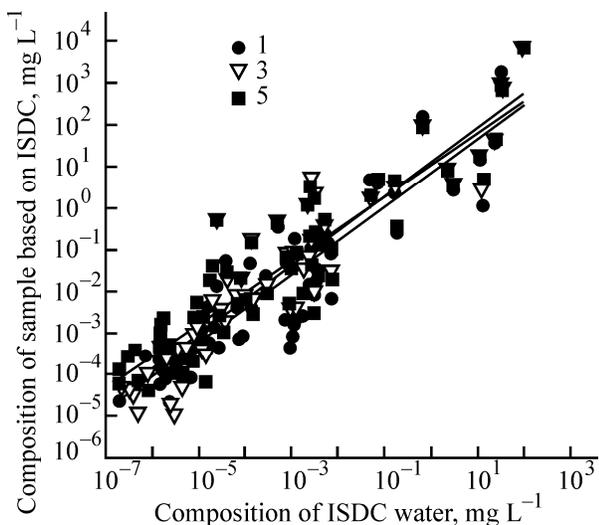


Fig. 1. Ratio of microelement concentrations in water of the industrial shower drainage channel of the Beloyarsk Reservoir (ISDC) and in sample nos. 1, 3, and 5 after introducing into natural water 1-, 3-, and 5-mL aliquots of multielement solutions prepared from monazite, respectively. The log-log regression lines for the natural water composition in comparison with the artificially prepared water after introducing aliquots of increasing volume are shown. Point nos. are water sample nos.

sorption selectivity of plankton is one of the factors disturbing the ^{234}U - ^{238}U and ^{230}Th - ^{234}Th radioactive equilibrium in freshwater basins [18, 19]. This fact makes plankton a promising biosorbent for both radioactive and stable isotopes of elements in aquatic ecosystems [3].

The fate of dying plankton in water in the context of the transfer of a significant fraction of the sorbed chemical elements into bottom sediments is still poorly understood. In particular, it is unclear whether high levels of element uptake by plankton ensure the water self-clearance as a result of the transfer of elements into bottom soil with the dead plankton [2, 3, 20]. For correct estimation of the flows of elements, including radionuclides, in the water-biota-bottom sediments system, it is necessary to know to what extent the live and dead plankton differ in the ability to take up chemical elements from freshwater basins. Answering this question involves a methodical problem: It is necessary to estimate small changes in the concentrations of elements constituting the natural background in water against the background of the supply of the same elements in the course of natural dying-off of the biosorbent. The urgency of the experimental solution of this problem is caused by significant role of plankton

as biosorbent in assimilation and transfer of the chemical elements accumulated by the whole plankton biomass along food chains of the water body, taking into account gradual dying-off of plankton, and by the need to have quantitative data on this process in freshwater ecosystems [2, 4].

This study was aimed at experimental evaluation of the sorption of some macro- (Mg, Ca) and microelements (Sr, Ba, Mn, Fe, REE, Th, U) by live and dead plankton at different concentrations of these elements in aquatic medium. Experiments were performed under natural temperature-controlled conditions in the summer period using water and natural plankton taken from the cooling pond of the Beloyarsk NPP.

EXPERIMENTAL

The investigation objects were water and plankton from the Beloyarsk Reservoir, an artificial freshwater basin in the Middle Urals [2]. The reservoir was formed in 1959–1963 by controlling the waterway of Pyshma River; it acts as cooling pond of the Beloyarsk NPP.

In our experiments on sorption of elements by biota in natural waters, we proceeded from the need for making the artificially created sorption conditions maximally close to the natural conditions in the concentration levels of separate introduced elements and in their ratio. To this end, water samples were filtered through a blue band paper filter and were placed in vessels, and into each of them the elements under consideration were introduced in the form of an aliquot of the solution obtained after dissolving a 0.05-g portion of monazite (cerium-lanthanum phosphate containing cerium group elements, uranium, and thorium as impurities [21]). The monazite weighed portion was preliminarily dissolved in sulfuric acid, after which the acid was distilled off, and the REE salt residue was dissolved in water [14]. The ratio of chemical elements similar to their ratio in natural water was created in the solutions (Fig. 1). This approach allowed us, using aliquots of the solution obtained from the monazite weighed portion, to create in the experiment the element ratio that increased from sample to sample and was qualitatively similar to the natural ratio of the elements in water from the Beloyarsk Reservoir. Introduction of microelements in one aliquot allowed us to increase the concentration of all the artificially introduced macro- and microelements (Mg, Ca, Sr, Ba, Mn,

Results of determining the Langmuir isotherm parameters from data on the sorption of chemical elements by samples of live (v) and dead (m) plankton. Student's test $t(k = 12, \alpha = 0.05) = 3.055$ [26]; k , number of degrees of freedom; α , level of significance; $T(k)$, statistical similarity test in accordance with expression (1); SE, standard error of K_d

Element	$T(k = 12)$	$K_d(v), \text{ml g}^{-1}$	$E(v), \text{mmol g}^{-1}$	$K_d(m), \text{mL g}^{-1}$	$E(m), \text{mmol g}^{-1}$	SE(K_d)	
						(v)	(m)
Mg	16	852	0.2	6667	0.1	1.4	357
Ca	781	1655	33.2	956	33.4	0.7	0.5
Sr	642	1069	1.5×10^{-3}	653	1.43×10^{-3}	0.6	0.1
Ba	56381	36295	5.0×10^{-4}	3418	6.40×10^{-4}	0.5	0.3
Mn	0.1	4.5×10^6	0.1	1624	0.1	5.2×10^7	4600
Fe	2.6	8191	0.1	471	1.5×10^3	2900	152
Pr	1227	29898	6.1×10^{-5}	448	4.50×10^{-5}	24	0.1
Th	979	36425	2.41×10^{-4}	2377	5.6×10^{-5}	34	2.6
U	546	1156	37.5	679	4.4×10^{-5}	0.9	0.1

Fe, REE, U, Th) to the level exceeding the natural background of these elements in the reservoir by a factor 10–60 by varying the aliquot volume. Such approach decreased the overall preparative errors of the experiment, including inevitable change in pH. According to the thermodynamic estimation of the chemical composition of element ions introduced into water of the Beloyarsk Reservoir (HSC Chemistry program, Module v.8.1) and to our previous data, the main species of Mg(II), Ca(II), Sr(II), and Ba(II) are simple aqua ions; Mn(II), Fe(II), La(III), Pr(III), and Th(IV) mainly exist as hydroxo complexes; and U(IV), as carbonate complexes [22, 23]. These ionic and molecular species will interact with the plankton at pH of the experiment. Along with ionic species, microamounts of Th(IV) and U(VI) tend to form colloids of sorption type, which have the particle size of $>0.1 \mu\text{m}$ and do not participate in the sorption process [24].

Plankton for the experiment was taken from the water body adjacent to the nuclear power plant (region of the industrial shower drainage channel, ISDC) from the depth of 0–1 m using hand nets fabricated from milling gauze with a mesh size of 0.064 mm. After water draining, a part of the wet mass of the plankton was placed in the previously prepared vessels with solutions of the elements under consideration. The other part of the plankton was placed for 2 min in a UHF furnace at a power of 600 W and a temperature of 95°C, after which the sample of the plankton killed by such treatment was used in a similar experiment. The pH values in the experimental solutions were 7.2–8.3.

After the completion of the experiments, the plank-

ton was separated from water by filtration through a membrane filter with a pore size of $1 \mu\text{m}$ [25] and was dried. Samples were dissolved in a 2 : 1 : 1 mixture of nitric, hydrochloric, and hydrofluoric acids and were kept in an autoclave for 15–30 min at 150–160°C with the subsequent calcination for 2 h in a muffle furnace at 450°C.

Quantitative determination of the elements was performed on a Perkin–Elmer SCIEX quadrupole mass spectrometer (USA–Canada) using a calibration standard solution with the required range of the element concentrations. The relative standard uncertainty of the determinations did not exceed 10–20%.

For comparative estimation of the accumulation of chemical elements by the live and dead plankton, we used the distribution coefficients ($K_d, \text{mL g}^{-1}$) and the sorption capacity ($E, \text{mmol g}^{-1}$), which were calculated per air-dry plankton mass from the sorption isotherms. The sorption isotherms were constructed from the results of experiments with variable concentrations of elements in water samples, and the parameters of the Langmuir sorption model were found (see table). The morphological analysis of the plankton samples was performed by transmission electron microscopy with a JEOL JSM 6390 LA device equipped with a JEOL-23010 BU attachment for local energy-dispersive elemental analysis. Nanocomposite track membranes with a pore size of $0.5 \mu\text{m}$ were used as supports.

RESULTS AND DISCUSSION

Figures 2–5 show the isotherms of sorption of chemical elements by samples of live and dead plank-

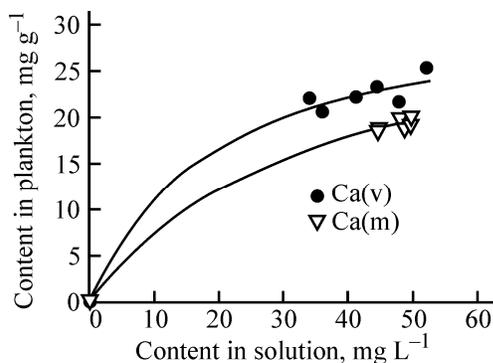


Fig. 2. Isotherms of sorption of Ca(II) ions introduced into natural water by samples of live (v) and dead (m) plankton. 24°C; the same for Figs. 3–5. Lines: approximation of the experimental data using Langmuir equation; the same for Figs. 3–5. Here and in Figs. 3–5, the element concentrations in water after plankton separation and in plankton cells at a water–plankton contact time of 4.5 h are shown.

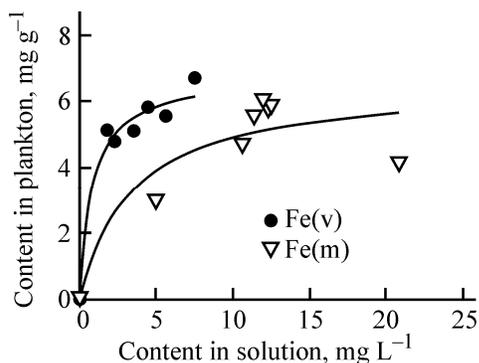


Fig. 3. Isotherms of sorption of Fe(II) ions introduced into natural water by samples of live (v) and dead (m) plankton.

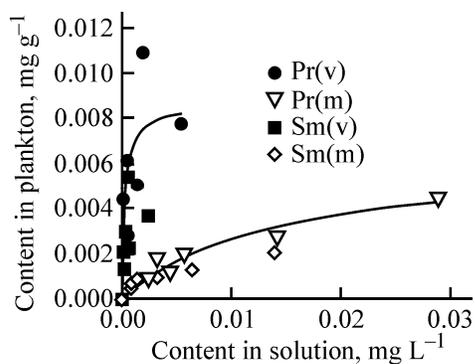


Fig. 4. Isotherms of sorption of Pr(III) and Sm(III) ions introduced into natural waters by samples of live (v) and dead (m) plankton.

ton after the experiment completion. Analysis of the sorption parameters using the Langmuir model allowed us to obtain the set of physicochemical characteristics reflecting the sorption properties of live and dead

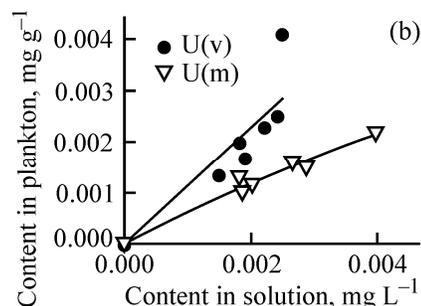
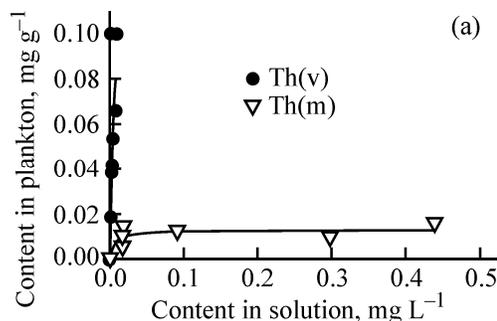


Fig. 5. Isotherms of sorption of (a) Th(IV) and (b) U(VI) by samples of live (v) and dead (m) plankton.

plankton under the conditions close to natural conditions (K_d , E) and to reveal qualitative and quantitative differences in the sorption activity of live and dead plankton. Figure 6 shows that the majority of elements under consideration are taken up by the live plankton with higher distribution coefficients than by the dead plankton. The exceptions are Mg(II) cations, for which the pattern is inverse.

The experimentally determined sorption capacities (E , mmol g^{-1}) of plankton samples are given in the table. These data also indicate that the sorption capacity of the live plankton for all the elements studied (except Mg ions) is higher than that of the dead plankton.

It is also important to evaluate the statistical significance of the difference between the live and dead plankton in the sorption affinity for the elements under consideration. To do this, we checked, using Student's $T(k)$ -test, the simple statistical hypothesis that the estimated mean values, $K_d(v)$ and $K_d(m)$ (data for live and dead plankton, respectively), for separate chemical elements are equal. According to [26], the hypothesis $H(0)$ is formulated as follows: For a chosen element sorbed by the plankton, the distribution coefficients for the live and dead plankton are statistically equal, $K_d(v) = K_d(m)$. The hypothesis $H(0)$ is checked by comparing the $T(k)$ test for the similarity of the distri-

bution coefficients for the live and dead plankton (1) at statistical number of the degrees of freedom k ,

$$T(k) = |K_d(v) - K_d(m)| / \{ (SE)^2[K_d(v)] + (SE)^2[K_d(m)] \}^{-1/2}, \quad (1)$$

with the tabulated value of Student's test $t(k, \alpha)$ for the significance level $\alpha = 0.05$. If

$$T(k, \alpha) > t(k, \alpha), \quad (2)$$

hypothesis $H(0)$ is rejected; otherwise, it is assumed for the chosen significance level α . In Eqs. (1) and (2), $k = 14 - 2 = 12$ for the experimental conditions, and $(SE)^2[K_d(v, m)]$ is the squared standard error of estimating the distribution coefficients of a microelement for samples of the live and dead plankton, found by the least-squares treatment of the Langmuir isotherms (see table).

As seen from Fig. 7, the calculated values of $T(k)$ for the majority of chemical elements considerably exceed the Student's test. This fact indicates that the difference between the live and dead plankton in the distribution coefficients of elements is statistically significant. The manganese distribution, for which these differences are insignificant according to our estimation, is an exception.

In the course of direct microscopic studies of plankton samples using local X-ray fluorescence analysis, we were able to reveal among the whole set of plankton cells the cells characterized by especially high manganese content. After the exposure under the electron beam of the microscope with the energy of 2–3 eV in a high vacuum, we found that these cells mainly consist of three elements: oxygen, manganese, and carbon (Fig. 8). Their chemical composition is close to the formula MnO_2C , and their morphology fully repeats the morphology of *Trachelomonas acanthostoma* var. *acanthostoma* Stokes (sensu Swir. et Defl.) plankton cells [27]. The revealed plankton cells are saturated with ions or coated with a thin layer of manganese compounds. Apparently, *T. acanthostoma* var. *acanthostoma* microalga is a specific manganese accumulator [28]. However, the biomass of this microalga at the moment of analysis was as low as ~0.15% of the total plankton biomass, and its contribution to the overall ability of the plankton to accumulate manganese is insignificant.

Thus, we have experimentally estimated the distribution coefficients of a number of elements for live

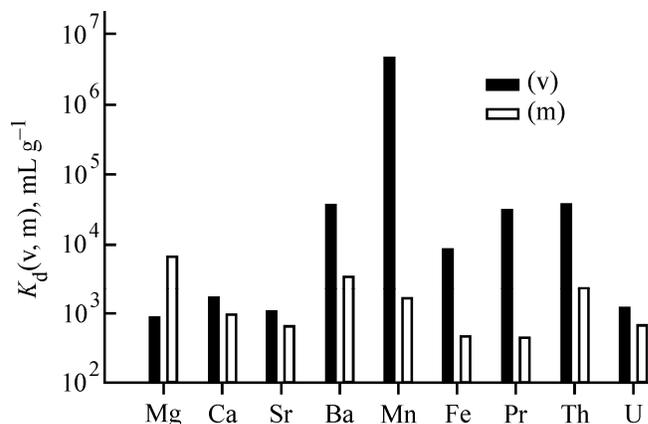


Fig. 6. Comparison of K_d values of elements, obtained for samples of live (v) and dead (m) plankton by estimation of sorption parameters using Langmuir equation.

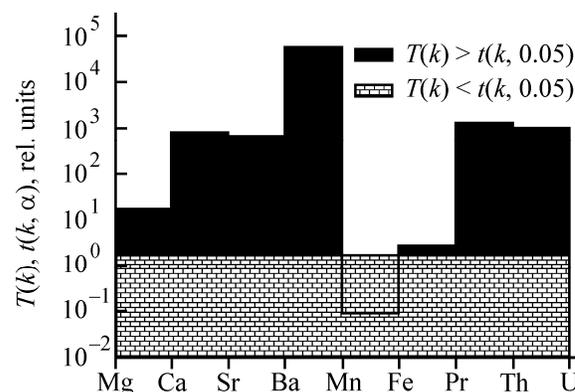


Fig. 7. Results of checking hypothesis $H(0)$ that the distribution coefficients of elements, found using Langmuir sorption model, are equal for cells of live (v) and dead (m) plankton. ($T(k)$) Test for the similarity of the distribution coefficients for live and dead plankton at the number of degrees of freedom k (1).

and dead plankton of ISDC of the Beloyarsk Reservoir. It was shown for plankton as biosorbent that the sorption isotherms of the macro- (Mg, Ca) and microcomponents (Sr, Ba, Mn, Fe, REE, Th, U) follow the Langmuir equation and that the distribution coefficients of the elements, except Mn, for the live and dead plankton differ statistically significantly. The latter fact is consistent with the results of previous studies [29, 30]. With respect to the sorption affinity ($\log K_d$ [mL g⁻¹] ~3–5), freshwater plankton is an effective biosorbent. Therefore, it is promising to use it not only for biogeochemical indication of the pollution of natural water bodies, but also as a natural biosorbent for use under emergency conditions. From this viewpoint, the difference between the live and dead plankton in

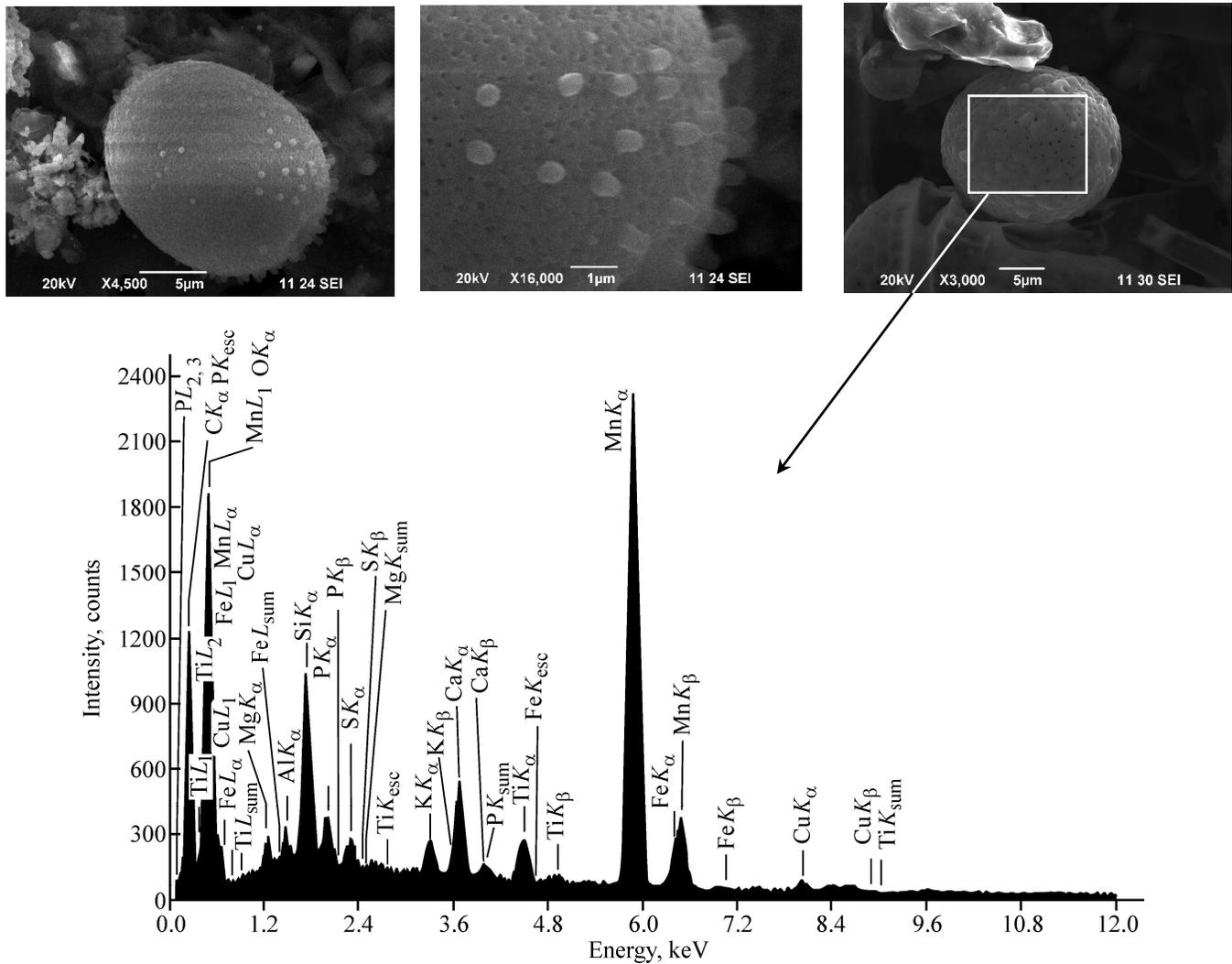


Fig. 8. Electron microscopic image of a sample of plankton cells at different magnifications; below: X-ray fluorescence spectrum of a plankton cell noted with a quadrangle.

the K_d values, revealed in this study, shows that the technology for treatment of contaminated water with this biosorbent should take into account the plankton lifetime in the course of preconcentration and the rate of the plankton renewal. Otherwise the treatment becomes less efficient. Electron microscopic examination with local multielement analysis revealed for the first time abnormally high manganese content for a freshwater plankton species, *T. acanthostoma* var. *acanthostoma*, in the cooling pond of the Beloyarsk NPP.

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