# **Bottom Sediments of Surface Watercourses of the Malmyzhsky Mountain Range**

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**Abstract**—Using the methods of X-ray fluorescence, electron microscopic, sedimentation analysis, and laser diffractometry, the composition of bottom sediments of surface watercourses in the Malmyzhskaya Ridge section allocated for the construction of a mining and processing enterprise (Khabarovsk krai, Russia) was studied. It was established that the bottom sediments of the coastal zone of the watercourses of the studied region are characterized by a similar gross composition and physical and chemical properties (pH, solid phase density, total carbon content, contact angle CAW). They are mainly represented by a fine soil with a high portion of suspended sediments, in the composition of which the coarse silt fraction prevails (particle size  $\leq$ 2 mm,  $\leq$ 0.1 mm, and 0.01–0.05 mm, respectively). It was demonstrated that deforestation in the sources of watercourses (accompanied by soil erosion) leads to a significant increase in the dispersion of sediments (an increase in the portion of suspended sediments up to 90%) in the upper reaches. The effect of afforestation on the dispersion of sediments fades downstream with the distance from the felling sites. The content of suspended sediments decreases to the values typical for watercourses, on the catchment area of which no deforestation was carried out. A significant microaggregation of the suspended sediments of watercourses was detected, and the involvement of microbiota (testate amoebae of xenosomic taxa, diatoms, and Fe-reducing bacteria) was diagnosed in the formation of microaggregates. The latter are involved in the formation of vivianite on the surface of ferruginous–clay microaggregates with an increased content of phosphates after fires. A mechanism for the formation of toroidal microforms of vaterite in the bottom sediments with the involvement of cyanobacteria from the *Spirulinaceae* family was proposed.

**Keywords:** deforestation, soil erosion, bottom sediments, vivianite, vaterite, Malmyzhskaya Ridge, Russian Far East

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## INTRODUCTION

The bottom sediments of surface watercourses are an important source of information about the environmental conditions in the catchment area and are traditionally used as an indicator for the identification and estimation of the intensity and scale of technogenic load. The dynamics and composition of sediments are closely related to the processes of soil erosion in the catchment area, both natural and technogenic (as a result of mining, open pit mining, construction of roads, forestry, etc.). The technogenic load intensifies

the rate of soil erosion by from one to two orders of magnitude as compared with natural background indices (Dymov, 2017; Dymov et al., 2022; Brandon, Pinter, 2005; Golosov, Wolling, 2019; Owens, 2022). The bottom sediments play an important role not only in the accumulation of a number of macro- and microelements, but also in the formation of a selfcleaning capacity of the watercourse and receiving water reservoirs (Förstner, Wittmann, 1983).

Until the beginning of the 21st century, the territory of the Malmyzhsky mountain range (Far East,



**Fig. 1.** Schematic map of the studied region: (*1*) site boundaries, (*2*) sampling places, and (*3*) afforestation areas.

Russia) experienced almost no technogenic load, with the exception of the construction of roads to settlements (the towns of Verkhnii Nergen and Malmyzh) and logging, which were accompanied by laying of portages and logging roads. The situation changed dramatically after the discovery of the Malmyzhskoe gold–copper–porphyry deposit in 2006. The geological additional exploration and estimation of the reserves of the main ore components (2018–2020) demonstrated that this is a world-class deposit that is poor in content (about 0.35% on average) of copper reserves. The Russian Copper Co. decided to construct a mining and processing enterprise. The project for the deposit development and extraction of copper concentrate involves the use of flow technologies in open-pit mining (during the transportation of rock mass) and step-by-step grinding of ore (to a grain size of 0.030 mm) followed by flotation of the "ore" dust. After the project realization (2024–2025), the power of mining and processing enterprise should reach the processing of 90 million t of ore per year and production up to 250 thousand t of copper in a concentrate (Maksimov, 2021; *Dragotsennaya med' …*, 2022).

At the initial stage of the development of the Malmyzhskoe gold–copper–porphyry deposit and the construction of a mining and processing enterprise and objects of a technological complex (quarries, overburden dumps, tailing, etc.), afforestation was carried out locally in the upper reaches of watercourses (Fig. 1). It is known that afforestation in the catchment area leads to a significant increase in the rate of soil erosion, surface runoff, flow, and inflow of sediments (suspended material) into the bottom sediments of watercourses. The sediment inflow from watersheds is mainly determined by the rate of soil erosion upstream and is maximally manifested in the first years after afforestation (Brandon, Pinter, 2005; Horton et al., 2017; Owens, 2022).

The aim of this work was to study the peculiarities of the composition and dynamics of the bottom sediments of surface watercourses in the Malmyzhskaya Ridge section allocated for the construction of a mining and processing enterprise and the effect of afforestation in the upper reaches of watercourses on the soil erosion and sediment runoff at the initial stage of the construction. This is a continuation of our studies

of the Amur and its tributaries (Chizhikova et al., 2011; Sirotskii et al., 2014; Kharitonova et al., 2019, 2020). In this article, the bottom sediments of small watercourses before the beginning of the development of the Malmyzhskoe gold–copper–porphyry deposit are considered.

## MATERIALS AND METHODS

The works were carried out in the lower reaches of the on Amur River the watercourses of the Malmyzhsky Mountain Range (Nanaysky district, Khabarovsk krai). Climatically, the considered territory belongs to the Bolonsky district of the Middle Amur province, which is part of the monsoon forest climatic region (Alisov, 1969; Petrovi et al., 2000). The effect of monsoon processes on the climate formation in this territory is most clearly manifested. In the second half of summer, warm and humid sea air is transported here from the Pacific Ocean with tropical cyclones (typhoons). Summer can be characterized as warm. Due to the inflow of cold air masses with northern and northwestern currents, winter is cold or very cold.

According to long-term data, the average annual precipitation varies from 500 to 700 mm. Winter is long (135 days) and severe. It comes at the beginning of November, and its arrival is accompanied by a sharp decrease in air temperatures and strong winds. Cloudless frosty days are established for a long period. The soils freeze to a depth of 2.0 m and more.

The relief of the territory belongs to a low-mountain (altitudes up to 300–345 m) medium dissected erosion–denudation type. In geological and orographic terms, the Malmyzhsky Mountain Range is a continuation of the Sikhote-Alin. Its northwestern slopes are characterized by a significant steepness (up to 35°–40°) and are dissected by numerous steep slopes of temporary watercourses. The slopes of the southeastern exposure (gentler and longer) are complicated by the spurs of the southeastern direction formed by rather deep valleys of small watercourses with a subparallel flow direction.

The territory allocated for the construction of a mining and processing enterprise includes the basins of the rivers flowing into the floodplain Amur lakes Kaltakheven, Bol'shaya and Malaya Sharga, and Dzhalunskoe. These are lakes of a rather large floodplain–channel expansion of the Amur River, which further downstream is pinched by small hills: from the left bank, the Bolon heights; from the right bank, the Malmyzhskaya Ridge. The region that we are studying (Fig. 1) is located within a mountain range that is small in size with brown forest soils under cedar– deciduous forests. It includes the basins of the rivers flowing into the lakes Bol'shaya and Malaya Sharga: the Biha (7.5 km), Kupchu (7 km), and Yao (11 km) rivers and the Glubokii and Kholodnyi streams. The watercourses originate from the Malmyzhskaya Ridge,

flow in a southern direction, and are characterized by rather large slopes, small length, and low tortuosity. The river valleys of small watercourses within the mountainous territory are consistent with tectonic disturbances and fracture zones of the Earth's crust. In this case, the valleys become straight for a considerable length and have a V- or box-shaped profile with steep slopes. The floodplains in these watercourses are absent or, in some places, form narrow fragments up to several tens of meters wide.

The rivers belong to the Manoma-Gursky subdistrict and, according to the conditions of water regime, belong to the Far Eastern type, for which a well-pronounced predominance of rain runoff is a characteristic feature. They are distinguished by a flood regime during the entire warm period and a relatively high runoff in the winter period (a result of the effect of groundwater). The mountain character and climate of the territory causes instability of soils to mechanical effects and the activity of river bed processes.

The bottom sediments of the main small watercourses of the construction site of the Malmyzhsky mining and processing enterprise was the study object. Sampling was carried out in July 2020 after afforestation in the upper reaches of the watercourses at the initial stage of the construction, before the beginning of the deposit development, which allows to classify the state and properties of the sediments as conditionally unchanged. Nine samples were taken in the coastal zone of water objects: point 1, Lake Malaya Sharga, low southwestern coast (49.862° N 136.941° E); point 2, Lake Malaya Sharga, elevated northwestern coast (49.872° N 136.920° E); point 3, Biha River, middle course (49.893° N 136.884° E); point 4, Kupchu River, middle course (49.903° N 136.938° E); point 5, Yao River, upper course (49.921° N 136.984° E); point 6, Glubokii stream, upper reaches (49.954° N 137.024° E); point 7, Glubokii stream, lower reaches (49.904° N 137.044° E); point 8, Kholodnyi stream, middle course (49.924° N 137.057° E); and point 9, Polen River, lower reaches (49.884° N 137.045° E). Previously obtained results of the analysis of the composition and properties of bottom sediments of the Simmi River (Bolonsky Reserve) (Kharitonova et al., 2020) on the left bank of the floodplain-channel expansion of the Amur River were used for the comparison.

When selecting, standard equipment and methods were used (*Nastavleniya …*, 1975; *Rukovodstvo …*, 2012). The main study methods (granulometric and gross chemical analyses, scanning electron microscopy (SEM analysis)) were supplemented by standard physicochemical methods (Vadyunina, Korchagina, 1973; Shein et al., 2017). The granulometric composition was determined by a sedimentation method (mass distribution) according to Kaczynski, and the microaggregate composition was determined by a laser-diffraction method (volume distribution) (Rawl, 2014). Laser diffractometry of the samples was performed on

Selection point	$pH_{water}$	$pH_{salt}$	$\textbf{W}_{\rm{hygr},\%}$	$\rho$ , g/cm <sup>3</sup>	$S, m^2/g$	CAW, deg	$C, \%$
	5.2	3.9	1.55	2.65	2.4	58.5	1.16
$\overline{2}$	5.2	4.3	2.88	2.65	7.2	31.1	1.33
3	5.2	3.9	3.00	2.49	5.4	44.3	1.75
$\overline{4}$	6.6	4.3	3.38	2.32	8.9	45.1	1.54
5	5.2	4.3	3.67	2.54	5.2	56.4	2.35
6	5.4	3.9	2.99	2.67	6.4	48.8	1.73
7	5.0	3.8	4.30	2.55	6.1	50.3	3.31
8	5.2	3.8	6.63	2.35	2.1	60.1	8.12
9	5.2	3.8	2.50	2.57	6.5	53.2	1.55

**Table 1.** Physicochemical characteristics of bottom sediments of watercourses of the Malmyzhsky mountain range

ρ, solid phase density; S, specific surface according to N<sub>2</sub>; CAW, contact angle; C, carbon content in the fraction <0.25 mm.

a particle-size analyzer SALD-2300 (flow cell) (Shimadzu, Japan). For this purpose, a water suspension of the sample (the sample depends on the absorption of the obtained suspension and is at the average from 0.5 to 1 g) was treated with ultrasound for 10 s before the analysis (built-in ultrasonic disperser for sample homogenization). SEM analysis was performed using a VEGA 3 LMH scanning electron microscope (TESCAN, Czech Republic). For imaging, the samples (preliminarily ground and sieved through a 2-mm sieve) were prepared by a spilling method and sputtering with Pt, with a magnification up to 20000 $\times$ . To analyze the phases with a high atomic number, a backscattered electron (BSE) detector was used in addition to a secondary electron (SE) detector. When imaging with a BSE detector, phases with a high average atomic number are reflected more clearly in contrast as compared with the phases with a lower atomic number. To analyze the elemental composition of the most representative regions, an X-max 80 energy dispersive spectrometer (Oxford Instruments, United Kingdom) was used. The gross composition of air-dry samples was determined by an X-ray fluorescence (XRF) method on a Pioneer S4 Bruker AXS instrument (Germany) according to a silicate method. SEM and XRF analyses were performed at the analytical center of the Institute of Tectonics and Geophysics, Far East Branch, Russian Academy of Sciences (Khabarovsk). A specific surface was determined by a low-temperature nitrogen adsorption method on a specific surface analyzer of the SORBTOMETER-M series, and  $C_{org}$  was determined by a coulometric titration method in an oxygen flow on an AN-7529-M express carbon analyzer (Gomel, Belarus). A contact angle was measured by a static drop method using a DSA 100 drop-shape analysis system (KRÜSS, GmbH, Germany) (Tyugai, Milanovskiy, 2015).

## RESULTS

A brief physicochemical characteristic of the samples is presented in Table 1. According to the obtained data, the bottom sediments of the studied region are characterized by similar physicochemical properties (pH, solid phase density, total carbon content, contact angle CAW). The coastal sediments of the Lake Malaya Sharga and the sediments of the Kholodnyi stream (p. 8) were an exception. Compared with others, the bottom sediments of the Kholodnyi stream (p. 8) are distinguished by an increased content of  $C_{\text{tot}}$  $(8.1\% \text{ with an average content of } 1.9\%);$  this is associated with a high content of transportable fine detritus. Removal of the latter before the analysis without the loss of mineral components was not possible. Due to the flowing nature of the region and the effect of floods (in the forward and reverse directions), the bottom sediments of the northwestern shore of the lake (p. 2) are characterized by increased hydrophilicity. The contact angle of wetting the sediments in p. 2 was 31.1°, with the average values in the studied region being 51.2°.

Except for the coastal sediments of the Lake Malaya Sharga (p. 1, low southwestern shore of the lake, remnant of an ancient sandy coastal ridge of the Amur River) with an increased content of  $SiO<sub>2</sub>$ , the sediments of watercourses of the Malmyzhskaya Ridge are also characterized by close values of the gross chemical composition (Table 2). Thus, taking into account the losses during ignition, the standard deviation of the content of  $SiO<sub>2</sub>$  and  $Al<sub>2</sub>O<sub>3</sub>$  does not exceed 2%, or 0.4% of other oxides of macroelements. We note that the content of  $Fe<sub>2</sub>O<sub>3</sub>$  in the sediments is almost five times higher than that of CaO (3.9 and 0.8%, respectively, average values).

Data on the granulometric composition of the sediments that characterize the conditions of sediment accumulation and their ability to be transported by

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Selection point	SiO <sub>2</sub>	TiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MnO	CaO	MgO	Na <sub>2</sub> O	$K_2O$	LOI	$P_2O_5$
											mg/kg
	74.88	0.35	10.99	2.43	0.04	0.67	1.22	2.77	2.62	4.40	870
$\overline{2}$	67.43	0.55	12.74	3.24	0.07	0.90	0.98	3.03	2.50	9.43	1200
3	65.98	065	13.67	3.27	0.06	0.77	1.27	3.13	2.38	9.42	860
4	62.78	0.74	15.59	4.61	0.08	0.52	1.18	2.22	2.89	9.98	1140
5	63.28	0.71	13.46	4.16	0.07	0.82	0.99	2.87	2.40	11.96	1220
6	60.60	0.70	14.01	3.45	0.05	0.83	0.97	2.78	2.25	16.16	1130
7	64.98	0.70	13.93	3.81	0.06	0.75	1.07	3.45	2.53	9.06	810
8	65.99	076	13.05	3.83	0.11	0.87	1.06	2.74	2.02	9.18	1740
9	65.14	0.71	12.98	4.47	0.11	0.86	0.80	3.45	2.31	9.52	1450

**Table 2.** Gross composition of bottom sediments of the watercourses of the Malmyzhskaya Ridge, %

LOI, loss on ignition.

**Table 3.** Distribution of particles in bottom sediments of watercourses of the Malmyzhskaya Ridge, %

Number of sampling points	Fraction size, mm									
	${<}0.1*$	< 0.01	< 0.001	$ 0.001 - 0.005 $ 0.005 - 0.01		$0.01 - 0.05$	$0.05 - 0.25$	$0.25 - 1$		
	30.40	16.67	9.00	3.89	3.78	18.82	39.09	25.42		
$\overline{c}$	60.70	24.86	12.96	11.02	0.88	39.38	23.60	12.16		
3	88.50	30.85	11.11	9.12	10.62	52.08	17.07	0.00		
$\overline{4}$	91.20	59.32	13.55	22.10	23.67	33.82	5.58	1.28		
5	77.80	39.37	15.06	14.64	9.67	37.53	22.68	0.42		
6	92.40	44.94	17.44	22.88	7.62	47.90	7.16	0.00		
7	79.70	41.02	17.25	13.53	10.24	42.70	16.28	0.00		
8	75.70	51.12	18.29	19.82	13.01	40.35	8.53	0.00		
9	83.60	32.23	15.72	14.15	2.32	59.93	7.84	0.00		

\* Suspended sediments, microaggregate composition (laser-diffractometry method).

water flow (including the processes of removal and accumulation of suspended sediments as a result of technogenic load) are significantly more variable. According to the obtained data (Table 3), the sediments of the coastal zone of watercourses are mainly represented by fine soil (particle size  $\leq$ 2 mm) with a high portion (up to 90%) of suspended sediments (particle size  $\leq 0.1$  mm). In their composition, the coarse-silt fraction of  $0.01-0.05$  mm (up to  $60\%$ ) predominates. At the same time, a fine-sand fraction of 0.05–0.25 mm (39%) prevails in the sediments of southwestern part of the coastal zone of the Lake Malaya Sharga (p. 1). Its content is also high in the sediments of northwestern part of the lake (p. 2), but the coarse-silt fraction predominates as at other sampling

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points. The content of suspended sediments in the lake sediments is 30 and 61% (pp. 1 and 2, respectively).

The sediments of the rivers Biha, Kupchu and the Glubokii stream, in the upper reaches (pp. 3, 4, and 6, respectively), in the sources of which afforestation was performed, are characterized by the highest content of suspended sediments (88–92%). In addition, pp. 3 and 6 that are closest to the felling sites were also distinguished by a maximal water turbidity as compared with other sampling points. It is important to note that the effect of afforestation on the dispersion of sediments fades with a distance from them. The turbidity decreased downstream with distance from the felling sites, and the content of suspended sediments decreased to the values noted in the Kholodnyi stream

(up to  $76-80\%$ , pp. 5, 7, and 8, respectively), in the catchment area of which no afforestation was conducted. Even taking into account the natural spatial variability of the indices, data obtained indicate that there is a reverse course in the distribution of sediment dispersion downstream (longitudinal profile) of watercourses as a result of afforestation.

We note that the portion of fine and medium silt fractions is significantly higher in the sediments of the Kupchu River (p. 4) as compared with the sediments of the Yao River (p. 5), (22 and 24% in the first case and 15 and 10% in the second case, respectively). Since the felling affected a significant part of the Kupchu River sources, felling was carried out in a similar area in the catchment area of the Yao River were carried out above its sources. A similar trend was noted for a pair of the Glubokii stream and Biha River (pp. 6 and 3), for which the total content of fine and medium silt fractions in the sediments of these watercourses was 30 and 20%, respectively.

#### DISCUSSION

Data on the granulometric and microaggregate compositions of the bottom sediments of watercourses of the Malmyzhskaya Ridge section allocated for the construction of a mining and processing enterprise (and, first of all, on the content of suspended sediments in them (up to 90%)) demonstrate high rates of soil erosion and sediment runoff as a result of afforestation in the sources of watercourses in the first year after felling (Biha and Kupchu rivers, Glubokii stream). This is also indicated by a reverse course of the distribution of sediment dispersion down along the longitudinal profile of watercourses. The effect of a similar influence of forest felling on the soil erosion and sediment runoff is well known for the basin of the Amazon River and its subbasins with annual precipitation from 2000 to 4000 mm/year (Golosov, Wolling, 2019). According to long-term data, the average annual precipitation in the study region does not exceed 700 mm. Apparently, the observed effect of high rates of the soil erosion and sediment runoff as a result of clear felling in the studied territory is determined by an erosive capacity of precipitations (one of the key driving factors of water soil erosion), as a result of monsoon processes (summer influx of typhoons and, accordingly, strong and continuous showers).

Visualization of the composition of watercourse sediments by SEM methods indicates that, in addition to primary minerals represented by clastogenic grains from 50 to 500 μm in size, they contain a significant amount of microaggregates out of silty particles and clayey–silty microaggregates up to 50 μm in size (Figs. 2a, 2b). In the sediments of the Polen River, particles of finely dispersed detritus (Fig. 2c), on which vivianite discharges were diagnosed (Fig. 2d), were also involved in their formation. Previously, we

found similar discharges in the sediments of the Simmi River (left bank of the Amur River) after the autumn–spring fires, which can indicate with a high degree of probability that there have been recently in the Polen River basin.

Diatoms were diagnosed in the lake sediments in the composition of microaggregates. Moreover, pennate diatoms dominate under conditions of a slow flow (p. 1), while centric diatoms dominate in the area with a higher flow rate (p. 2), (Figs. 2e, 2f). Testate amoebae of xenosomal taxa with the tests constructed out of mineral particles also make a certain contribution to the formation of microaggregates. Since the nature of the tests reflects a sedimentological composition of the environment (du Châtelet et al., 2015; Qin et al., 2017), xenosomes are mainly represented by silty particles (Figs. 2g, 2h). No involvement in the formation of microaggregates of idiosome taxa, the tests of which consist of secreted biosilicon particles (biomorphic silica) and organic coating (Figs. 3a–3c) was recorded.

The sediments of the Polen River (p. 7) are characterized by the highest relative abundance of xenosomal taxa. As has been demonstrated by studies (du Châtelet et al., 2015; Qin et al., 2017), fires lead to significant changes in the testate amoeba community and to a shift in the balance in favor of xenosomal taxa. A direct destruction of the organic coating of idiosome tests at extremely high temperatures is the most probable explanation for this shift after the fires. It is considered that the representatives of xenosomal taxa are more resistant to physical and chemical decomposition. The taxa with idiosome tests prevailed in the bottom sediments of the rivers, the catchment areas of which were not subject to the fires (Figs. 3a–3d).

The discovery of cyanobacteria of the *Spirulinaceae* family in the bottom sediments of the studied region (an unnamed tributary of the Kupchu River) (Fig. 3e) allowed one to explain the appearance and suggest a mechanism of formation of  $CaCO<sub>3</sub>$  discharges uncharacteristic for bottom sediments of the humid zone (vaterite mesocrystals) (Fig. 3f). Vaterite is formed at the first stage of calcium-carbonate precipitation; in contact with water, it is extremely unstable and transforms into calcite at a room temperature. Until recently, it was considered that vaterite does not form mineral forms under natural conditions. Rare cases of its formation were registered in the zones of thermal metamorphism and when carrying out drilling operations (Friedman, Schultz, 1994). The detected mesocrystals have a toroidal shape (with a diameter of about 10 μm and a cross-sectional radius of about  $1 \mu m$ ). They consist of flat microcrystals with a thickness of 0.1–0.2 μm and a diagonal/diameter of 1–2 μm, and their "plane-to-plane" packing with an angular shift leads to the formation of symmetrical volumetric structures (mesocrystals toroidal in shape).



**Fig. 2.** Microphotographs of typical microaggregates of the bottom sediments of the studied watercourses: (a) from silt particles (p. 4, Kupchu River); (b) from clay and silt particles (p. 5, Yao River); (c, d) with the involvement of fine detritus (p. 9, Polen River); selected area, vivianite discharges; arrow, EDS analysis in the point; (e, f) microaggregates with the involvement of pennate and centric diatoms (Lake Malaya Sharga, pp. 1 and 2, respectively); and (g, h) "microaggregates" of testate amoebae (pp. 7 and 9, Glubokii stream, lower reaches, and Polen River, respectively). (SEM, BSE detector).

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**Fig. 3.** Microphotographs of microbiota of bottom sediments of the studied watercourses: (a–c) idiosomal testate amoebae (p. 2, Lake Malaya Sharga; p. 4, Kupchu River; p. 8, Kholodnyi stream, respectively); (d) xenosomic testate amoebae (p. 8, Kholodnyi stream); (e) cyanobacteria of the *Spirulinaceae* family; and (f) mesocrystal of vaterite of toroidal shape (p. 3, Biha River). SEM, BSE detector.

Cyanobacteria of the family *Spirulinaceae* are notable for the formation of coiled trichomes (strands of hundreds of cells connected by intercellular interactions). The diameter of the helix coil is from 4 to 10 μm; the thickness of trichomes varies from 1 to 2 μm. As demonstrated by the studies of K. Konhauser and R. Riding (2012), a discharge of mineral forms of  $CaCO<sub>3</sub>$  is typical precisely for cyanobacteria of this family. This occurs as a result of selective adsorption of calcium cations by the functional groups of exopolysaccharides secreted by the cells of cyanobacteria and their subsequent interaction with carbonate ions. For clarity, we present a simplified, somewhat modified scheme by Konhauser and Riding, in which the involvement of bicarbonate ions of the external solution in cell photosynthesis is not taken into account (Fig. 4a). It should be noted that cyanobacteria contain polypeptides containing low-molecular-weight amino acids Arg (arginine) and Asp (aspartic acid). A similarity of the shape and size of natural mesocrys-



**Fig. 4.** Scheme of the formation of mineral forms on the surface of bacterial cells:

(a) Cyanobacteria; (b) Fe-reducing bacteria. EPS, exopolysaccharides; L, anionic ligands; thick dash, adsorption of  $Ca^{2+}$  cations and Fe(OH)<sub>3</sub> hydroxides; dashed arrow, interaction with carbonate and phosphate (silicate, sulfate, sulfide, and bicarbonate) anions of external solution (Konhauser and Riding, 2012).

tals of vaterite and helix coils of cyanobacteria of the family *Spirulinaceae* and the ability of the latter to biomineralize  $CaCO<sub>3</sub>$  allows to assume with a high degree of certainty that they are involved in the formation of toroidal forms of vaterite in the bottom sediments. The biological mechanism of the formation of  $CaCO<sub>3</sub>$ toroids is also supported by their A right-sided (counterclockwise) helical morphology (Fig. 3f), which is inherent in L-homochirality of natural amino acids and biomolecules (Jiang et al., 2017), indicates in favor of biological mechanism of the formation of  $CaCO<sub>3</sub>$  toroids. In addition, the scheme of Konhauser and Riding also describes one of the possible mechanisms for the formation of vivianite in the bottom sediments (Fig. 4b).

As has been demonstrated by W.S. Jiang et al. (2017), toroidal microforms of vaterite with a hierarchically organized architecture are formed under laboratory conditions *ex situ* in the presence of chiral L- and D-amino acids Asp and Glu. "Laboratory" toroids had a diameter of up to 50 μm and a cross-sectional radius up to 15 μm. High concentrations of used reagents (as compared with natural ones) are be the most probable reason for such a significant difference in the size of vaterite discharges. Second, the experiment was carried out under static conditions. We note that we found the toroidal microforms of  $CaCO<sub>3</sub>$ *in situ* not only in the sediments of the Biha River. Previously, they were diagnosed in river and peat sediments (the Amur River basin, Khabarovsk krai), with the age of the latter being more than 6000 years (Bazarova et al., 2018). Apparently, the formation and stability of toroidal microforms of vaterite (not only under laboratory conditions, but also under natural ones) are associated with the presence of low-molecular-weight amino acids.

#### **CONCLUSIONS**

The studies of material composition of the bottom sediments in the Malmyzhskaya Ridge section allocated for the construction of a mining and processing enterprise demonstrated that the bottom sediments of the coastal zone of watercourses of the studied region are characterized by a close gross composition and physicochemical properties (pH, solid phase density, total carbon content, contact angle CAW). Data on the granulometric and microaggregate composition of sediments, which characterize not only the conditions of accumulation of suspended sediments (particle size <0.1 mm) and their ability to be transported by a water flow, but also the processes of soil erosion in the catchment area as a result of afforestation, are distinguished by a significantly greater variability.

The sediments of the Biha and Kupchu rivers and the Glubokii stream (upper reaches), in the sources of which afforestation was carried out, are characterized by the highest content of suspended sediments (88– 92%). As compared with the rest, these sampling points also differed in an increased water turbidity. As a distance from the felling sites increases, the effect of afforestation on the dispersion of sediments fades, and there is a reverse course of changes in the dispersion of sediments down the longitudinal profile of watercourses. Downstream, the content of suspended sediments decreased to the values of 76–80% typical for watercourses, in the catchment area of which no afforestation was carried out (the Glubokii stream, lower reaches, and Kholodnyi stream, respectively). Data obtained indicate high rates of soil erosion and sediment runoff as a result of afforestation in the sources of watercourses (Biha and Kupchu rivers, Glubokii stream) in the first year after felling.

The bottom sediments of the studied region with a high portion of suspended sediments and a predominance of coarse silt fractions in their composition are characterized by a relatively high degree of microaggregation. In addition to primary minerals (represented by clastogenic grains with a size from 50 to 500 μm), they contain a significant amount of microaggregates out of silty particles and clay–silty microaggregates with a size up to 50 μm. The involvement of microbiota (pennate and centric diatoms and Fe-reducing bacteria) was diagnosed in the formation of microaggregates. The latter are involved in the formation of vivianite on the surface of ferruginous–clay microaggregates with an increased content of phosphates after fires. The testate amoebae of xenosomal taxa also make a certain contribution to the formation of microaggregates. Since the nature of the tests reflects the sedimentological composition of the medium, xenosomes are mainly represented by silty particles.

The discovery of cyanobacteria of the *Spirulinaceae* family in the bottom sediments of the studied region (an unnamed tributary of the Kupchu River) allowed one to explain the appearance and propose a mechanism for the formation of  $CaCO<sub>3</sub>$  discharges (vaterite mesocrystals, formations of a toroidal shape with a diameter of about 10 μm and a cross-sectional radius of about 1 μm) that are uncharacteristic for the bottom sediments of the humid zone. A similarity of the shape and size of natural mesocrystals of vaterite and helix coils of cyanobacteria of the family *Spirulinaceae*, the ability of the latter to biomineralize  $CaCO<sub>3</sub>$  allows one to assume with a high degree of certainty that they are involved in the formation of toroidal forms of vaterite. A right-handed (counterclockwise) helical morphology, which is inherent in the L-homochirality of natural amino acids and biomolecules, testifies in favor of a biological mechanism of the formation of  $CaCO<sub>3</sub>$  toroids.

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#### COMPLIANCE WITH ETHICAL STANDARDS

This article does not contain any studies involving animals and human beings performed by any of the authors.

#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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