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The arsenic spreading over thallus of *Saccharina latissima* of different habitats of the Barents Sea

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Abstract. The algae *Saccharina latissima* (Phaeophyceae) and bottom sediment were studied in two places of its habitat in the Zelenetskaya Bay of the Barents Sea: 1) in the zone of shipping traffic and ship parking (ZST&SP) and 2) algae plantations (AP) - the background part of the bay. According to the results of scanning electron microscopy and micro-X-ray spectral analysis, an active new formation of framboidal pyrite, iron oxides-hydroxides, and salt crystals were founded in the bottom sediment in the ZCST&SP of the bay. In the structure of the rhizoids of the thallom algae, inclusions of bottom sediment particles were revealed. The ICP MS method showed that the arsenic content in the *S. latissima* thallom significantly exceeds its level of presence in the bottom sediment. The maximum content of arsenic in algae from both habitats is determined in the rhizoids, and the lowest in the young part of the plate (meristem). The bottom sediment and thallom of *S. latissima* from the ZCST&SP contain two to three times more arsenic than the algae on the plantation.

1. Introduction

The algae *Saccharina latissima*, formerly belonging to the genus "kelp" - Laminaria saccharina, is widespread in the sublittoral zone of the Barents Sea. Its reserves are about 300 thousand tons. For many years, saccharina was the only object of algae fishery, it was used in food in the form of salad, as well as raw materials for obtaining alginate, mannitol, fucoidan, a pigment-lipid complex for medical biotechnology, and the creation of dietary supplements.

A big problem with the use of saccharina and kelp algae in the food industry, the creation of dietary supplements is the high content of arsenic in the thallus of algae. In recent years, there has been a lively discussion in the literature about the need to divide the detected arsenic in macrophyte algae into 2 groups: an organic form (arsenic is not hazardous to health) and an inorganic form (hazardous when consumed). Until now, questions have been raised about the mechanisms of arsenic accumulation by the saccharin thallus, the dependence of the arsenic concentration in the thallus on its content in the environment, and the spreading of arsenic over the plate.

The purpose of our work was to determine the concentration of arsenic in various parts of the saccharin thallus, the content of arsenic, depending on the conditions of the habitat.

2. Material and methods

Algae *Saccharina latissima* aged 1+ were selected for experiments in August 2020 at two points in the Zelenetskaya Bay of the Barents Sea. The first sampling point was located 3 meters from the operating berth, the parking lot of the small fleet (69°07′103″ n. longitude 36 ° 04′05 ″ e.latitude). A diver at a depth of 4 meters collected samples separating them with a knife from stones covered with muddy soil, rhizoids with a petiole and a plate of algae going to the surface of the water. The second point is the location of the artificial plantation with S. latissima algae: 69°07′08″ n. longitude. 36°04′35″ e.latitude area of the seasonal biological station MMBI RAS. Thalli aged 1+, 1.2-1.5 m in size, were collected from the horizontal rope of the plantation, which was fixed in the surface layer of water. Earlier, in July 2019, rhizoids of these thalli aged 0+ (young sporophytes) and sized 10-15 were woven into the rope. Thus, during a year of development, the rhizoids of these thalli were facing the water surface, and the plate grew from the surface to the bottom. The depth of immersion in the water of the horizontal rope was 20-50 sm, and the distance to the bottom was about 8 meters. Thalli collected at two points (without signs of sporulation) were delivered to the laboratory, where they were cleaned of fouling, washed with seawater, and dried at room temperature. Then the thalli were divided into parts: the rhizoid, the petiole, the meristematic zone of the plate close to the apex of the petiole (the beginning of the leaf), and the edge of the leaf. In parallel with the algae in the place of their growth, soil was taken: at the pier (depth 4 m), and under the plantation - a depth of 8 meters.

The sediment structure was determined by granulometric analysis on a standard set of sieves. The mineral composition of the bottom sediment was studied using the scanning electron microscope with a micro-X-ray spectral analyzer (Hitachi S-3400N). The determination of arsenic content in samples of bottom sediment and talom was carried out in a certified laboratory of the Geological Institute (VSEGEI). Samples of the bottom sediment were ground to an analytical powder, fused with lithium metaborate, dissolved in a mixture of acids and analyzed by the IMP MS method. The talom samples were dissolved in aqua regia and analyzed by the IMP MS method.

3. Results

The bottom sediments of the Zelenetskaya Bay of the Barents Sea are sand, siltstone and clay. The sediment of the background part of the bay is represented by fine-grained classes of fineness (more than 60 rel. % clay dimension). Sediment in the zone of permanent shipping traffic and parking of ships (ZST&SP) along with fine grain classes (less than 30 rel. % clay) contains particles of silt-sand dimension (Figure 1.).

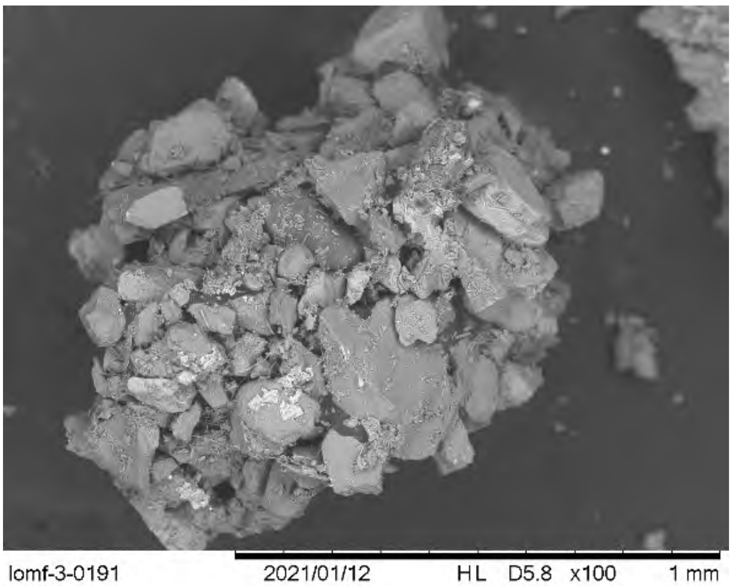

Figure 1. Clay-silt-sand sediment of the ZST&SP part of the bay.

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According to the results of scanning electron microscopy and micro-X-ray spectral analysis, an active new formation of framboidal pyrite (Figure 2), iron oxides (Figure 3) and salt (Figure 4) was found in the bottom sediment of the ZST&SP bay. Only salt crystals (NaCl) were found in the sediment of the background bay.

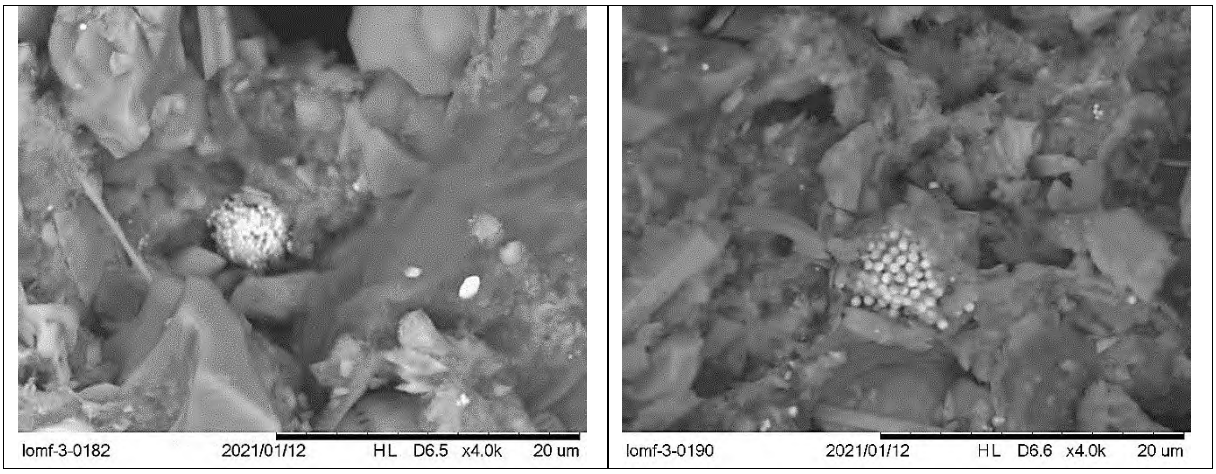

Figure 2. Framboidal pyrite concretions.

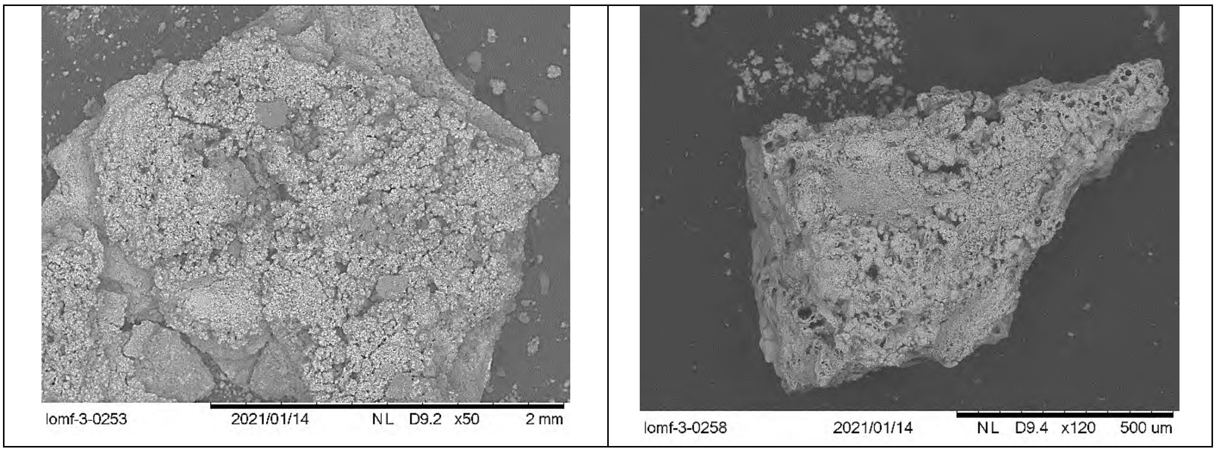

Figure 3. Iron oxide-hydroxide crus.

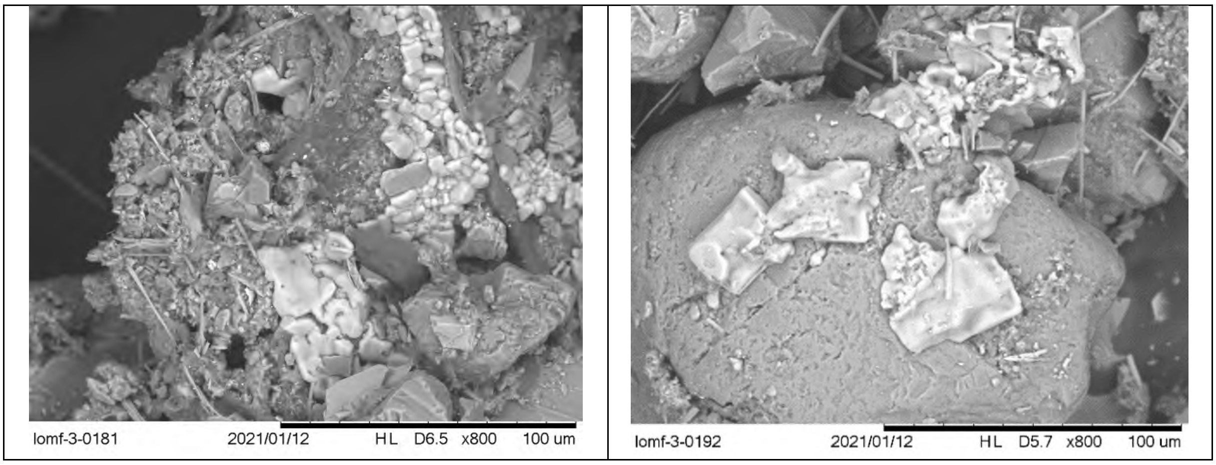

Figure 4. Salt crystals (NaCl).

The crust of iron oxides-hydroxides contains molybdenum, nickel and cobalt. In addition to sodium and chlorine, the salts contain potassium and bromine. Alumosilicates with admixture of calcium, magnesium, sulfur and phosphorus were found in the clay component of the sediment.

The highest content of arsenic: 127 mg/kg was found in the rhizoids of saccharina taken for analysis in the area of the pier. In rhizoids, saccharins from the plantation contain 57.2 mg/kg. In the petioles of saccharin growing near arsenic 64.4 mg/kg is also more than in the petioles of algae from the plantation: 45.2 mg/kg. In the meristematic tissue (the young part of the plate), the arsenic content from the berth area is 62.3 mg/kg, and in similar samples from the plantation, it is 59.5 mg/kg. The content of saccharin in the extreme (old) part of the plate in samples taken near the berth is 97.9 mg/kg, and from the rope of the plantation - 52.0 mg/kg. In sediment samples taken near the pier, the arsenic content is 5.80 mg/kg, and 3.46 mg/kg under the plantation.

4. Discussion

Members of the genera Saccharina and Laminaria have a large surface area and a high level of windage. This is the reason for the need for these algae to have a branched system of rhizoids, which form a "bottom" at the point of contact with the substrate. Quite often, both the "bottom" and a large number of individual rhizoids are covered with a layer of sediment. After the destruction of the plate in the one-year thallus, saccharins in the autumn period, rhizoids, petiole and the transitional part from petiole to plate (meristematic tissue) remain intact. It is due to the intensive division of meristem cells from the end of January to April that the active formation of a new plate takes place, with the movement of old cells along the periphery of the plate. Thus, at the time of the selection for saccharina analyzes, the oldest part of the thallus was the rhizoids, and the youngest part was the growth zone near the petiole.

Therefore, it is possible that the presence of the greatest amount of arsenic, a number of heavy metals discovered by us and other authors (1, 2, 3, 4, 5) in saccharina = kelp rhizoids is due to the age of this part of the thallus. At the same time, the data obtained and the results of our earlier studies on the Spitsbergen (2019) suggest that the high level of arsenic in rhizoids (127.0 mg/kg) is due to its high content in the bottom sediment (5.8) and the ability of rhizoids to accumulate (absorb) arsenic as it goes with the roots of higher plants. According to a number of researchers (6), some representatives of aquatic macrophytes can be a root bioaccumulator. The correlation between the content of arsenic in marine water in the water area of algae habitat and the plants themselves is far from always present, which can be explained by intensive water exchange, especially in areas with tidal currents.

A significant number of newly formed mineral phases were found in the bottom sediment of the ZST&SP part of the bay. This may indicate an active change in the forms of chemical elements, in particular arsenic. Elements of the bottom sediment can pass into a mobile state and be absorbed by algae.

Conclusions

1. The sediment of the background part of the bay is represented by fine-grained classes of fineness (more than 60 rel. % clay dimension). Sediment in the area of shipping traffic and ship parking (ZST&SP) along with thin classes (less than 30 rel. % clay) contains particles of silt-sand dimension.

2. According to the results of scanning electron microscopy and micro-X-ray spectral analysis, an active new formation of framboidal pyrite, iron oxides, and salt (NaCl) was found in the bottom sediment of the ZST&SP bay. Only salt crystals were found in the sediment of the background bay.

3. According to the results of the ICP MS analysis, the bottom sediment of the background part of the bay contains arsenic in the amount of 3.5 mg/kg, and the bottom sediment in the ZST&SP zone-5.8 mg/kg.

4. Arsenic is found in various parts of the thallom of the alga Saccharina latissima in an amount of 45-127 mg/kg, which is significantly higher than the level of this element in the bottom sediment. The rhizoids contain 57.2-127 mg/kg, the petiole - 45.2-64.4 mg/kg, the young part (meristem) of the plate-59.5-62.3 mg/kg, and the old part of the leaf - 52-97 mg/kg. The highest arsenic content is typical for rhizoids.

5. The bottom sediment and tallow of Saccharina latissima in ZST&SP accumulates 2-2.5 times more arsenic than the tallow of algae on the plantation and the bottom sediment at the site of its production.

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