The role of fucus algae in bioremediation of coastal waters of the Barents Sea from oil products

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Abstract. There was estimated the contribution of Fucus algae to the removal of diesel fuel (DF) from the Kola bay of the Barents Sea. The calculations are based on the results of: 1) expeditionary observations of recent years of the reserves, distribution and biomass of fucoids of three parts of the bay and 2) laboratory studies of the ability of four types of fucus (Fucus vesiculosus, F. distichus, F. serratus, Ascophyllum nodosum) to neutralize the toxic effect of diesel fuel. It was shown that the reserves of fucus are 4720 tons of wet weight. The absorption capacity is maximum of F. vesiculosus, and decreases in the series of F. distichus ≥ F. serratus ≥ A. nodosum. The calculations showed that fucoids of the Kola Bay can absorb and recycle about 850 kg of diesel fuel in 5 days. The existing rows of Fucus algae of the Kola Bay are an important element in the implementation of preventive, everyday cleaning of the bay waters from oil products. The inclusion of data of the ability of other representatives of phytobenthos to neutralize DF could increase the role of algae macrophyte in cleaning the coastal marine water from oil products.

1. The Introduction

Previously it have been shown that fucus algae could be considered as the most resistable to the oil pollution among other representatives of phytobenthos of the Barents Sea. This can explain the survival of Fucus vesiculosus at the littoral of the Kola Bay under the constant influence of oil products (OP) at the layer of “chocolate mousse” near piers and onshore hydrocarbon processing plants. In the experiment on fucus and other species of algae there was demonstrated their ability to accumulate oil products from the marine water at the surface of thalli and to the following absorbing and neutralization of oil products in plants’ tissues. It was revealed that the decrease of the content of oil products in water proceeds in parallel with its increase in the thalli of algae. The destruction of oil products starts at the surface of algae because of epiphytic hydrocarbon oxidizing bacteria (HOB), then goes absorbing and neutralization of oil products by the cells of algae [1], [2], [3], [4], [5], [6].

In recent years there have been made the suggestions have been made of the possibility of using the marine algae-macrophytes for cleaning the coastal waters from oil products [3], [7], [8], [9]. To achieve these goals there have been developed and successfully tested the plantation-biofilter, based on the symbiotic association of algae and hydrocarbon oxidizing bacteria [2].
On the coast of the Barents Sea fucus algae along with laminaria form the highest biomass. However precisely on Fucus algae because of its habitat in the tidal zone, the main burden from exposure of toxicants lies on them.

A rough estimate of fucoid reserves in the Barents Sea was carried out more than 30 years ago. According to it the common reserves of fucoids are approximately 100-200 thousand tons [10], [11], [12]. The reserves in separate bays were estimated even more approximately because of the irregularity of observations, the inability to conduct the researches due to the location of the navy bases in the bays. At the same time, the knowledge of the distribution, the reserves of fucus algae, taking into account their sorption ability and detoxification of oil products allows to predict the contribution of these representatives of phytobenthos to the bioremediation of coastal waters, as well as the environmental consequences of decrease of their presence or total disappearance from the littoral zone.

The presented research has been conducted basing on the example of the Kola Bay, which is 57 km long and occupies one of the leading places in the Arctic in transportation and transshipment of oil products. On the shore of the Kola Bay hydrocarbon processing plants are under construction, which entails the expansion of the coastal zone with backfilling of the tidal part and dredging in others. The calculation of the possible role of Fucus in bioremediation of sea water from oil products is based on the results of expeditionary observations of recent years on the distribution and biomass of fucoids in three regions of the Kola Bay and laboratory researches of the ability of three types of fucus to neutralize the oil products.

2. Material and methods

2.1. Laboratory experiments
Vegetative algae thalli, approximately equal in size and weight, have been selected in the upper, middle (Fucus vesiculosus, Ascophyllum nodosum) and lower (F. serratus) horizons of the littoral of the Zelenetskaya Bay of the Murmansk coast of the Barents Sea (69°07′09″ N, 36°05′35″ E), these algae have been also cleaned from fouling and placed in glass containers (volume is 1,3 liters) with marine water. Marine water (salinity is 33 %) was pre-filtered through a cotton-gauze filter and there was also added the summer diesel fuel to it in an amount of 6.5 mg / liter, which is 130 MPC for water according to the gross content of oil products. The marine water and the diesel fuel hasn’t been sterilized. The experiment was conducted at thermostatic box at temperature of 7–8°C, lighting - 16–18 W / m2 and with constant aeration of water. The total duration of the experiment was 5 days. During the experiment, the changes of the state and morphology of thallus of algae were monitored visually and using a MIKMED-6 microscope. The total content of oil products in water and in thalli was determined by gas chromatography / mass spectrometry (GC / MS). Sample preparation and instrumental analysis were conducted according to the previously described method [3]. To assess the background level of oil products, there were analyzed the samples of water and algae from the Zelenetskaya Bay.

2.2. Assessment of reserves of fucus algae of the Kola Bay
The assessment of reserves was conducted according to the traditional methods [13]. The material was selected during the expeditions of the MMBI KSC RAS in 2009-2019 and the Russian Geographic Society. A large part of the coastline of the bay was inspected from the side of the vessel, which made it possible to compile a qualitative description of the distribution of macrophytobenthos, including determining the size of the fucoid row to assess their reserves. To determine the biomass of macrophytobenthos and individual species of algae, quantitative samples were taken by the method of trial plots laid along a transect perpendicular to the water edge. There were completed 11 such transects. The sample area is 0.5 × 0.5 m [11,14]. At each section, there were made stations on 6 horizons: the upper, the middle, and the lower horizons of the littoral (VHL, SGL, NGL, about 3.0, 1.5, and 0.5 m above the sea accordingly). The width of the row of the species was estimated on
average for a site of relatively vegetation in place. The length of littoral sections with certain community features was estimated using MapWiever 8.0. The topographic base is the contour of the coastline of navigational maps of the Kola Bay.

3. The results

3.1. The spreading, the reserves and the biomass of fucus algae of the Kola Bay: expedition and laboratory researches

There were considered four species of fucoids, which have spread uneven on the littoral of the Kola Bay. *Fucus vesiculosus* could be found everywhere, from the estuary of the Tuloma River to the estuary of the bay, using various substrates for attachment, including hydraulic structures. Its largest reserves are concentrated on the boulder littoral of the middle part, where the littoral width is more than 30 m, and biomass is located on the west coast to the south of the Bolshoi, Sredny, and Maly Olenyi islands 9.4 ± 0.3 kg / m². In the greater part of the littoral, the biomass of *F. vesiculosus* is about 1 kg / m², but due to the large area occupied by this species, its reserves are huge (table 1).

| Table 1. The reserves of fucus algae of the Kola Bay |
|-----------------------------------------------|
| Species | The reserves of fucus algae (tn - ton) of the Kola Bay | The northern part | The middle part | The southern part | Total |
|---------|-------------------------------------------------|------------------|-----------------|------------------|-------|
| *F. vesiculosus* | 303,9, 1547,1, 423,3 | 2274,3 |
| *F. distichus* | 398,3, 654,2, 907,1 | 1959,5 |
| *A. nodosum* | 86,0, 224,9, 60,5 | 371,4 |
| *F. serratus* | 113,5, 0, 0 | 113,5 |

The reserves, in wet weight, tn

| Species | The reserves of fucus algae (tn - ton) of the Kola Bay | The northern part | The middle part | The southern part | Total |
|---------|-------------------------------------------------|------------------|-----------------|------------------|-------|
| *F. vesiculosus* | 60,0, 310,0, 83,0 | 453,0 |
| *F. distichus* | 79,6, 131,0, 181,0 | 391,6 |
| *A. nodosum* | 17,0, 45,0, 12,0 | 74,0 |
| *F. serratus* | 22,7, 0, 0 | 22,7 |

*Fucus distichus* grows on the middle and lower littoral horizons of the whole Kola Bay. On steep rocks, especially this specie forms the fucoid row, but the biomass is not more than 1 kg / m². The greatest biomass was recorded on boulder coasts in the middle and northern parts of the bay - up to 6.9 ± 3.4 kg / m², but its reserves are concentrated in the southern part, where the species covers vast sandy coasts. The reserves of *F. distichus* of the Kola Bay are large and this species makes up the algae mass of the littoral communities along with *F. vesiculosus* (table 1).

*Ascophyllum nodosum* exists mostly on boulder coasts protected or weakly protected from wave impact; its thickets reach the significant growth at the leeward island. The high biomass of ascophyllum was found on the Catherine Island in the northern part of the Kola Bay, where it was 4.2 ± 0.8 kg / m². Separate small thalli are also noted throughout the bay. Representatives of *A. nodosum* are the inhabitants of the upper horizon of the littoral and during low tides this algae has been staid a dried state for a long time.

*Fucus serratus* is spread only in the northern part of the bay; its high biomass is 6.1 ± 1.5 kg / m², noted on the Catherine Island. Total reserves of *F. serratus* are only 114 tons. This is very small compared with other species: reserves of *A. nodosum* are three times larger, and *F. vesiculosus* is twenty times larger (table 1). At the same time biomasses of species of the northern part are comparable, and in the middle and southern the *F. vesiculosus* is significantly dominant. *Fucus serratus* grows in the lower horizon of the littoral and thalli are drained only at syzygy ebbs.
3.2. Potential contribution of Fucus algae to sorption and absorption of oil products in different regions of the Kola Bay: experimental and calculated data

The water taken in the habitat of Fucus algae at high and low tide had an average oil product content of 0.2 mg / L (4 MPC). The analyzes revealed insignificant differences in the oil product content in the control samples of Fucus: *F. vesiculosus* - 25 mgk / g, *F. distichus* - 24 mgk / g, *F. serratus* - 28 mgk / g, *A. nodosum* - 25 mgk / g.

The experiments showed that diesel fuel in marine water in concentration of 6.5 mg / l - 130 MPC does not affect harmfully on fucus. All the prototypes remained viable for 5 days of the experiment. Plasmolysis and other morphological changes typical in case of influence of alternating factors were not observed in the cells [15], [16], [17], [18].

As the result of the conducted experiment and chemical analyzes, the mass of absorbed oil products by 4 species of Fucus algae was determined in 5 days in conditions of temperature of water 8-10 ºC and the level of oil products in water - 130 MPC. This value was calculated basing on a dry weight of *F. vesiculosus*: 1036 mgk / g; *F. distichus*: 870 mgk / g; *F serratus*: 641 mgk / g; *A. nodosum*: 236 mgk / g.

| Species of algae | The northern part | The middle part | The southern part | Total |
|------------------|-------------------|----------------|------------------|-------|
| *F. vesiculosus*  | 62                | 321             | 86               | 469   |
| *F. distichus*    | 69                | 114             | 158              | 341   |
| *A. nodosum*      | 4                 | 11              | 42               | 19    |
| *F. serratus*     | 145               | 0,0             | 0,0              | 15    |

Total potential bulk of absorbed oil products by fucus algae of different parts of the Kola Bay for 5 days

During recalculating the obtained values for certain reserves of fucus algae of the Kola Bay (Table 1), taking into account wet to dry weight ratio of 5/1, there were obtained data on the potential bulk of accumulated and absorbed mass of oil products in different parts of the Kola Bay (Table 2).

Totally the potential contribution of fucus algae to the cleaning of the bay from oil products for 5 days was determined at 842 tons of oil products. Fucus algae make the maximum contribution to the neutralization of toxicants in the middle part of the bay, and the minimum - in the northern part (Table 2).

Among algae species, the greatest burden of neutralization of oil products in the middle part falls on *F. vesiculosus*, in the northern part this species shares the burden equally with *F. distichus*, and in the southern part *F. distichus* absorbs almost twice as much oil products as *F. vesiculosus*. Compared to the two species described, the contribution to the cleaning of the Kola Bay by *A. nodosum* and *F. serratus* is minimal and makes up less than 4% of the total oil products absorbed by algae.

4. The discussion

The Kola Bay of the Barents Sea was not chosen by chance as an experimental base. There is a real problem of oil pollution of the waters of the bay and it will not disappear in the near future.

The total content of dispersed oil products in the bay waters is on average 4-6 MPC. On the surface of the water, there are film forms of OP, which can be estimated from satellite images. According to the data of 2011-2014 the highest film density was recorded: near the objects of the Northern Fleet in the middle part of the eastern coast, at the estuary of the bay in the fairway area (ship spills), at a floating oil storage facility and in the port of Murmansk. The total area of film pollution throughout
the bay was 75-119 km². Since the surface of the bay is estimated at 175 km², 43-68% of the surface is contaminated [19]. According to Ilyin [20], in the middle part, the surface of the water is almost completely covered with a film of oil products. OPs are also found in water and bottom sediments; their concentration can reach 5 MPC or more. The main sources of oil pollution in the bay are oil storage facilities located almost along the entire coast, and oil transshipment terminals, the largest are located in the middle part. Our data and our previous studies [3], [6] showed that most of the bays of the Murmansk coast, including the waters of the Kola Bay, have background pollution of bays from 2 to 8 MPC (in case of absence of emergency spills).

The concentration of OP in the Kola Bay can constantly change due to the movement of water masses [21]. Simulation of the behavior of the oil slick during a spill in the middle part of the bay showed that at any speed, wind direction and air temperature, the OPs will be placed on the littoral [22].

Perennial Fucus algae dominate at the littoral of the Kola Bay. Apparently, a long stay in conditions of low pollution developed their resistance to higher concentrations of OP in water. This can explain the development of Fucus in our experiment without signs of damage at a concentration of oil products of 6.5 mg / L, and the existence of spills when Fucus survived but reduced functional activity when the concentration of OP in water was up to 50 mg / L [2]. Fucus algae, due to its habitat in the littoral zone, bear the main burden from exposure to pollutants, not only in the form of dissolved OPs, but also in the film deposited on the surface of the thalli of algae during low tides. Analysis of the expeditionary materials showed a great diversity in the structure and distribution of algae communities in the littoral of the Kola Bay. On the boulder coasts of large islands in the northern part of the bay, the most abundant species are *F. serratus* and *A. nodosum*. Here they form large reserves. *Ascophyllum nodosum* is widespread in the middle part of the bay, but here its biomass is significantly lower. In the southern part, almost 65% of the total reserves of fucus algae is occupied by *F. distichus*, *A. nodosum* no more than 5%, and the mass of *F. serratus* is negligible. The contribution of each species to the total biomass of algae in the reservoir must be known, due to the differences in sorption and absorption of OP by different types of algae shown [2], [3], [6]. The total reserves of fucoids in the Kola Bay are approximately 5 thousand tons, and approximately half are *F. vesiculosus* [23].

As our experiment showed, in natural conditions, at low concentrations of PP (background - 4 MPC), the absorption capacity of 4 types of fucus differs slightly. However, in the experiment at a concentration of 6.5 mg / L (130 MPC), the absorption capacity is maximal in *F. vesiculosus*, and then it decreases in the series *F. distichus ≥ F. serratus ≥ A. nodosum* (table 2). At present, we can only speculate on what these differences are due to: their structure, biochemical characteristics, or there may be a difference in the quantitative and (or) qualitative composition of hydrocarbon-oxidizing microorganisms in a symbiotic association.

The calculations showed that the fucoids available in the Kola Bay can absorb and convert about 850 kg of diesel fuel in 5 days in the warm season (from May till September). This is approximately 1 m³, which corresponds to a small spill and is comparable to chronic fuel leaks. According to preliminary results, when the experiment is continued up to 15 days, the efficiency of sorption and neutralization of OP by fucus algae increases.

In nature, the rate of absorption of OP by macrophytes, apparently, depends on hydrodynamics, water temperature, insolation, the characteristics of Fucus biology, the functioning of hydrocarbon oxidizing bacteria on the surface of algae. Therefore, our results on the possible participation of Fucus in bioremediation of the aquatic environment from OPs are preliminary. A fortunate coincidence is the fact that it is in the middle part, where the main sources of water pollution are located, large reserves of Fucus are concentrated.

The role of saccharin and kelp in algae bioremediation from oil products, as well as other representatives of the gulf flora, was not demonstrated in the presented work. Undoubtedly, taking into account the contribution, the role of phytobenthos in neutralizing the toxic effect of OP will significantly increase.
It can be unambiguously concluded that the existing Fucus algae of the Kola Bay is the important element (component, link) in the implementation of preventive, everyday cleaning of the bay waters from oil products.

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