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Composition, properties of Ahnfeltia biochar and the possibility of its use as a fertilizer for Luvic Anthrosols or for hydroponics

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Abstract: Recycling of beach macrophytes into biochar may be a good ecological solution for beaches where macrophyte management strategies are absent or irrational. Currently, large amounts of Ahnfeltia accumulate on some beaches in Primorsky Territory. The potential of recycling Ahnfeltia beach sediments in Primorsky Territory by pyrolysis for use as a fertilizer was assessed. Ahnfeltia biochar had a pH of 8.0±0.5, P_2O_5 was 365±12 mg/100 g, K_2O was 892±45 mg/100 g, and nitrogen was 8-10%. The water-holding capacity for the natural fraction was 432.5%, and for the fraction larger than 1 mm 630.4%. Ahnfeltia biochar had a higher value of water-holding capacity, plant nutrient content compared to wood biochar (Betula alba), which showed good results in Luvic Anthrosols (reduced CO_2 emissions, increased yield). Thus, we assumed that Ahnfeltia biochar can show a good effect on Luvic Anthrosols, as well as on soils with similar properties. It was shown that Ahnfeltia biochar actively saturates an aqueous solution with P_2O_5 and can maintain a stable concentration of P_2O_5 for three weeks when growing lettuce. This shows that Ahnfeltia biochar has the potential to be used in hydroponic installations as a fertilizer.
Keywords: *Ahnfeltia, Beach wrack, Biochar, Beach macrophytes.*

1. Introduction

There are many solutions for removing marine macrophytes from beaches. However, strategies for removing marine macrophytes from beaches are not always sustainable. The problem of removing macrophytes from beaches is relevant for recreational area owners worldwide. It is noted that the main strategy for removing marine macrophytes from beaches is removal and storage [1,2]. There are beaches where beach wrack management is absent. This is due to the absence of area owners. In such areas, marine macrophytes remain on the beach and rot. However, beaches with no marine macrophyte management strategies are a place for people to relax.

Primorsky Territory is located on the coast of the Sea of Japan and has an extended coastline. Primorsky Territory is often affected by powerful typhoons and cyclones, which result in large amounts of marine macrophytes being washed up on beaches [3]. The red alga Ahnfeltia is noted among beach marine macrophytes. There are no precise estimates of the amount of Ahnfeltia washed up on the beaches of Primorsky Territory. According to rough estimates, up to 5,000 tons of Ahnfeltia are washed up on the beaches of Peter the Great Bay (part of the Primorsky Territory coast) annually [4].

Ahnfeltia is a good agarophyte and is used to obtain agar, agarose, food and feed additives, fertilizers, and biostimulants in agriculture [5,6]. The chemical composition of Ahnfeltia varies depending on the growing location. However, it is claimed that organic fertilizers from Ahnfeltia are enriched with nitrogen, iodine, macronutrients, and micronutrients [5]. According to research, organic fertilizers produced from Ahnfeltia collected on the beach of Primorsky Territory have a positive effect on soil structure and plant development [7-9]. It was also noted that organic fertilizers from Ahnfeltia

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increased the mineral content in general and separately potassium, calcium, manganese, and iodine in watercress, lettuce, and cucumber [7-9].

Commercial reserves of Ahnfeltia in the Primorsky Territory are estimated to be about 45 thousand tons, while the production of the algae is about 1 thousand tons [10].

Most of the Ahnfeltia from the beaches of Primorsky Territory was used to produce agar [11]. To date, there are no large agar production facilities in Primorsky Territory [11]. There is also no continuous processing of Ahnfeltia into other raw materials. Thus, there is a problem of removing Ahnfeltia from the beaches of Primorsky Territory.

One of the ways to utilize Ahnfeltia from the beaches could be biochar. Biochar is a carbon-rich porous product with a unique structure that includes aromatic carbon compounds, many functional groups, high cation exchange capacity, and high specific surface area [12].

The properties of biochar determine its wide range of applications: soil improver, adsorption of heavy metals and organic pollutants, biological matrix, cosmetology, food industry, chemical industry, construction, energy, etc. [13,14]. Soil is the main application area of biochar. The positive effects of biochar on the biological, physical and chemical properties of soil are generally recognized and are observed in different soil and climatic conditions [12,15].

Recently, the use of various marine macrophytes as raw materials for biochar production has become widely popular [16,17]. Algal biochar has different properties from biochar from traditional biomass (agricultural waste, wood). Algal biochar has high surface area, cation exchange capacity, pH, Ca, P, K, Na, Mg, N content, but relatively low carbon content [18].

It is noted that algae biochars show high contents of N, P, K [19]. Since Ahnfeltia also has high contents of N, P, K and other macronutrients and micronutrients, we assume that Ahnfeltia biochar can be a good fertilizer.

The conversion of beach Ahnfeltia as well as other marine macrophytes into biochar can have environmental benefits: i) the removal of marine macrophytes from beaches can reduce greenhouse gas emissions that are released during their decomposition [2,20,21]; ii) biochar is a long-term carbon store [22]; iii) when used as a soil amendment, biochar can have the effect of reducing greenhouse gas emissions from the soil [15]. Research has shown that when implemented on a global scale by converting gigatons of biomass to biochar, it has the potential to mitigate global climate change by reducing greenhouse gas concentrations in the atmosphere [23].

In this paper we attempted to evaluate the potential of pyrolysis of beach Ahnfeltia as a potential fertilizer for Luvic Anthrosols or for hydroponics.

2. Materials and Methods

2.1. Biochar

The object of the study was algal biochar. Biochar was obtained from the alga Ahnfeltia tobuchiensis by medium pyrolysis in an inert nitrogen atmosphere.

Ahnfeltia tobuchiensis samples were collected in Baklan Bay, Primorsky Territory. Ahnfeltia is often found among beach wrack in Primorsky Territory. This is due to the large number of habitats of the alga at depths of up to 40 meters in the bays of Primorsky Territory [24]. Analysis of images from the Sentinel-2 satellite scanner to determine the area of emissions using the Q-GIS software package shows that the area of beach macrophytes on one of the beaches in Primorsky Territory varies in the range of 1.4×104–5.4×104 km^2 (Figure 1).

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Figure 1.
Ahnfeltia beach in the northern part of Baklan Bay on May 28, 2024 (Primorsky Territory).

After collection, the algae were air-dried for a week. The algae were pyrolyzed in a SAFTherm STZ 1214 furnace (Henan sante furnace technology co., ltd, China) in a nitrogen flow at a temperature of 500 °C for 30 minutes, the heating rate was 8.3 deg/min, and the nitrogen flow rate was 3 l/min. The yield of biochar from the pyrolysis of air-dried ahnfeltia was calculated using the equation 1 [25]:

$$\textbf{Biochar yield}, \% = \frac{W_{biochar}}{W_{seaweed}} * \mathbf{100}\ \% \quad (1)$$

where, $W_{biochar}$ is the weight of the biochar (g), $W_{biochar}$ is the weight of the initial seaweed (g).

Several samples of raw Ahnfeltia were pyrolyzed at 500 °C for 30 minutes. This was done to calculate the biochar yield from raw Ahnfeltia. The calculation of the biochar yield was carried out similarly to equation (Equation 1).

2.2. Determination of the Main Characteristics of Biochar

SEM images of crushed biochar were obtained using a scanning electron microscope Hitachi S-5500 ultra-high-resolution scanning electron microscope (Hitachi, Japan).

The pH of the aqueous extract and electrical conductivity were determined according to the standard method of Rajkovich et al. [26]. To determine the pH, the biochar was crushed and the fraction with a grain size of less than 1 mm was collected, which was then filled with 25 ml of distilled water and stirred for 60 minutes. After stirring, the pH and electrical conductivity were measured using a combined electrode and conductivity sensor from Mettler Toledo (USA).

The ash content of biochar was determined according to the standard method ASTM D1762-84 [27]. However, calcination of biochar at 750 °C for 6 hours did not result in complete combustion. Complete ash was achieved by burning biochar at 800 °C for 6 hours.

The determination of the organic carbon content of biochar was carried out according to two methods: wet combustion Walkley [28] and simultaneous determination of total carbon and nitrogen content Walkley, Black and Armstrong [29].

Fixed carbon (FC) content was calculated according to equation [30]. The method involved drying the biochar to constant weight at 105 °C to determine mobile compounds, heating for 10 minutes at 950 °C, and burning the sample at 800 °C for 6 hours to determine ash content. The fixed carbon (FC) content was calculated according to equation 2 [30]:

$$\mathbf{FC} = \frac{\mathbf{wt_{105} - wt_{950} - wt_{800}}}{\mathbf{wt_{105}}} \times 100\% \quad (2)$$

, where wt105 is the mass of biochar heated at 105 °C, wt950 is the mass of biochar heated at 950 °C for 10 min, wt750 is the mass of biochar calcinated at 800 °C for 6 h.

The total nitrogen content in biochar was determined using the Kjeldahl method [31]. Available forms of phosphorus and potassium in biochar were determined using the spectrophotometric method [32]. The content of heavy metals was determined according to Methods for the Examination of Composting and Compost [33].

The water-holding capacity of biochar was determined according to the method of Litvinovich et al. [34]. Biochar weighing 10 g was placed in glass flasks, 100 mg of distilled water was added and left for 4 days after which it was transferred to a funnel with a filter to remove excess moisture and then weighed. Moisture capacity for two fractions of biochar: the natural fraction and the fraction equal to less than 1 mm.

2.3 Determination of P_2O_5 release from biochar into aqueous solution

To assess the phosphorus supply to the solution, biochar samples were transferred to 5x7 cm tea filter bags made of water-permeable nonwoven material. The tea filter bags were brought into contact with 100 ml of distilled water for a total of 5 weeks. Two weeks after the start of the experiment, 10 lettuce sprouts were transferred to a glass of water. The content of available phosphates was measured at specified time intervals.

3. Results and Discussion

3.1. Properties of Ahnfeltia biochar

Figure 2 shows the images of the feedstock before loading into the pyrolysis furnace and the finished product. The feedstock is an elastic fibrous structure with irregularly shaped inclusions, presumably parts of other types of algae. The finished biochar retains its fibrous structure, but when mechanically impacted, it easily breaks into smaller particles. The yield of biochar from the pyrolysis of air-dried Ahnfeltia was 58.6±0.9%. The ash content value was 15.0±0.5%.

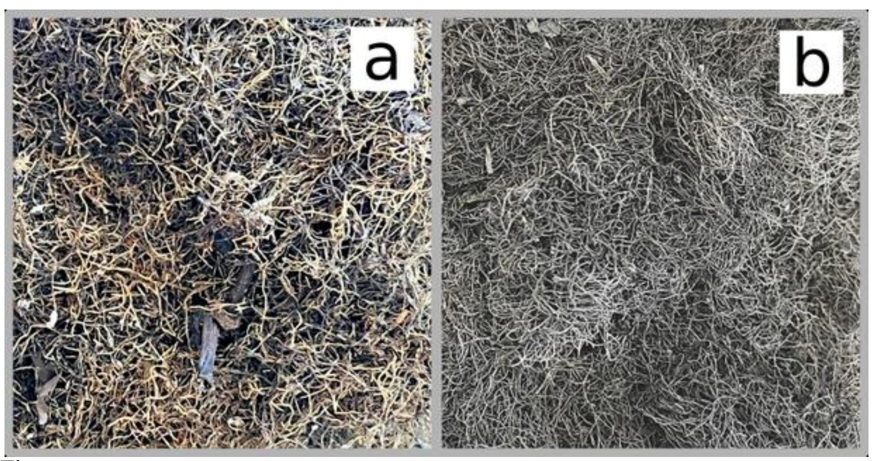

Figure 2.
Appearance of original Ahnfeltia (a), Ahnfeltia biochar (b).

Figure 3 shows SEM-images of the biochar. According to SEM-images, the crushed biochar sample was polydisperse particles of irregular shape containing pores with an average diameter of 3.3 μm. The pore geometry is irregular, the inner surface of the pores is rough. Oval inclusions with a diameter of 30 to 70 nm are noted on the inner surface of the pores.

Figure 4 shows the EDX spectra of biochar. The elemental composition of biochar at the fracture (figure 4a) is represented by a few elements, such as carbon, oxygen and sulfur, which are part of the carbonized residue, as well as sodium, magnesium, potassium, calcium and chlorine, which are the main components of seawater remaining after drying the sample. Elemental analysis of the inner part of the pores (figure 4b) showed an increased content of sodium and chlorine, which may be a consequence of

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the formation of halite crystals (NaCl) during pyrolysis, which are detected as rounded structures forming a rough surface.

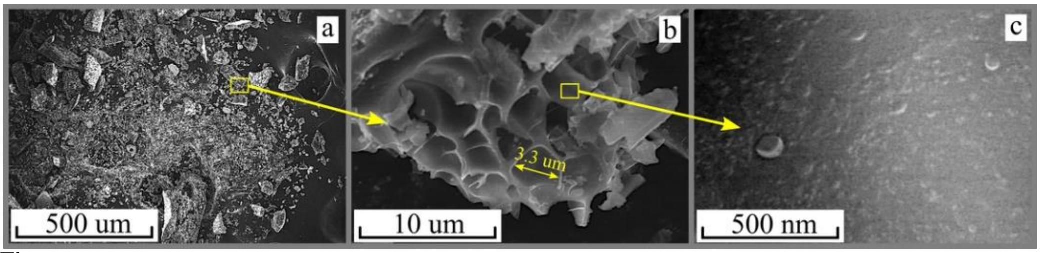

Figure 3.
SEM-images of the samples; magnification a – 100, b – x5.0k, c – x100.0k.

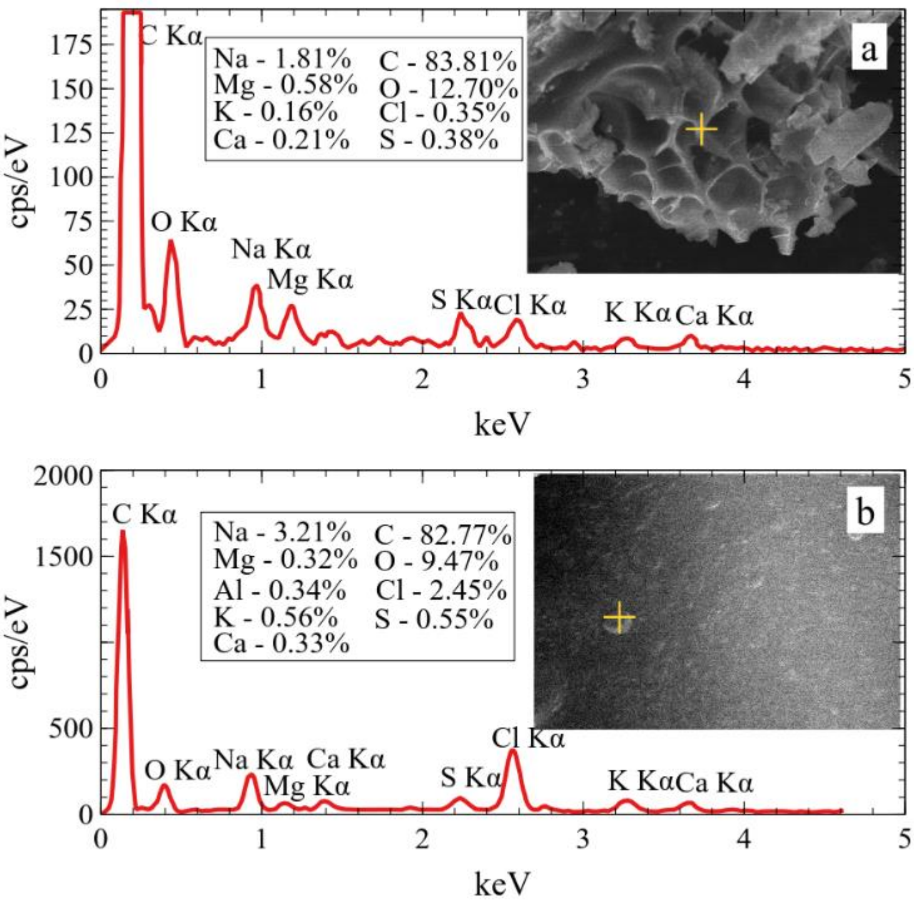

Figure 4.
Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX) analysis of Ahnfeltia biochar. Magnification a – x5.0k, b – x100.0k.

The pH of the aqueous extract varies in the range of 8 -10. Depending on the type of raw material, the pH of biochar varies from 3.1 to 13.7 [35,36]. Algal biochars have a pH of 7.6 to 13.7 [18]. Presumably, the alkaline reaction of biochar is due to the presence of alkali and alkaline earth metal carbonates, moderately soluble metal oxides and hydroxides, and silicates [37-41].

The presence of soluble salts in biochar as components of seawater remaining after drying of algae causes high electrical conductivity [42]. It is reported that the EC values of biochars can vary from 0.04

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dSm/m [43] to 54.2 dSm/m [44]. The biochar obtained in our study had an EC of 13.79 dS/m, which is an average value. It is noted that the application of biochars with high EC values to soil may adversely affect plants sensitive to increased mineralization [45].

Using the methods developed by Yeomans and Bremmer in 1988 [46] and Walkley and Black in 1934 [29], the organic carbon content ranges from 37–50% (Table 1). The results are consistent with previous data on the organic carbon content of algal biochar, which ranges from 28.5% to 59.2% [47].

Carbon content analysis using EDX-spectroscopy showed that its share in the sample is about 83±0.52% (Table 1). This is explained by the fact that the biochar may contain sodium, potassium and calcium carbonates that are stable at high temperatures. This is confirmed by the results of measuring the pH of the aqueous extract and the electrical conductivity value.

Table 1.
Characteristics of Ahnfeltia biochar.

Parameter	Value
Biochar yield, %	58.6±0.9
Ash, %	15.0±0.5
pH_{H2O}	8.00 ±0.5
EC, dS/m	13.79 ± 0.03
Total carbon content, EDX method, %	83.29 ± 0.52%
C_{opr} , % [44]	38-50
C_{opr} , % [29]	37-50
Total nitrogen content in biochar by the Kjeldahl method, %	8.0-10.0
P_2O_5 content in biochar, mg/100 g	365 ± 12
K_2O content in biochar, mg/100 g	892 ±45
Fixed carbon, %	41±2

Fixed carbon is an indicator of the amount of long-term carbon sequestration. In Ahnfeltia biochar its content was 41±2% (Table 1). Fixed carbon in biochars can vary from 0 to 77.4% and this is related to the type of biochar [30]. Maximum values of fixed carbon are shown in high temperature biochars with an ash content of less than 20%, with an increase in the ash content of biochar, the value of fixed carbon decreases [30].

To assess the suitability of biochar as a fertilizer, its heavy metal content was assessed according to the IBI (International Biochar Initiative) standard [32]. As shown in Table 2, the heavy metal content of Ahnfeltia biochar was lower than the minimum acceptable threshold, indicating that biochar is safe to use for growing crops.

Table 2.
Content of acid-soluble forms of heavy metals in Ahnfeltia biochar, mg/kg.

Element	Ahnfeltia biochar	IBI Standart
Zn	88.2	200-700
Cr	1.16	64-1200
Ni	2.08	47-600
Cd	0.19	1.4-39
Pb	0.27	70-500
Cu	4.09	63-1500
Co	1.79	40-150
Mo	0.01	5-20
Mg	66.00	-
Fe	115.00	-
Mn	275.00	-
Sn	0.32	-

In addition to heavy metals, the content of Mg, Fe, Mn and Sn was determined. Increased iron and manganese content was found in biochar, which is due to the geochemical anomaly in the content of these elements in rocks, soils and water of Primorsky Territory [48].

Biochar can retain moisture in sandier soils or remove some of the moisture in clayier soils. In this regard, the water-holding capacity of biochar was determined. The water-holding capacity of Ahnfeltia biochar for the natural fraction (>1 mm) was 432.5%, for the fraction less than 1 mm it was 630.4%. According to literature, these values of water-holding capacity are high. Thus, wood biochar can absorb no more than 285% of water [34].

3.2. Release of Available Forms of Phosphorus from Ahnfeltia Biochar Into Aqueous Solution

The release of phosphorus into the aqueous solution was relatively fast. In the first hour after adding biochar to the solution, an average of 2 mg/100 ml of P_2O_5 was released, after 24 hours the concentration of P_2O_5 in the aqueous solution was 6 times higher (figure 5). After 4 days, the release slowed down, and the content of available phosphates was up to 16.55 mg/100 ml. Thus, in 1 week, up to 22.07 mg/100 ml of distilled water was released. After placing ten lettuce sprouts in a solution with biochar, the content of available phosphates did not change over a period of 2 to 5 weeks and varied from 20 to 21 mg/100 ml.

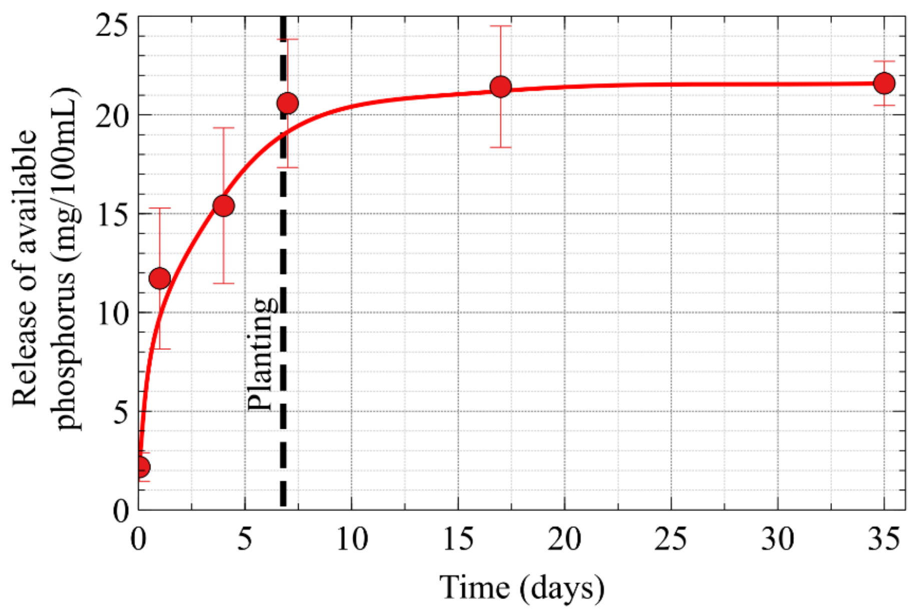

Figure 5.
Release of P_2O_5 from Ahnfeltia biochar into aqueous solution.

Biochar can actively interact with aqueous solutions, which allows it to be effectively used in hydroponics. It is noted that biochar can be an alternative raw material for hydroponic installations [49]. The efficiency of using biochar in hydroponics is associated with the stable carbon structure of biochar, its resistance to microbial decomposition and physicochemical properties [49]. When growing plants in hydroponics with the addition of biochar, an increase in the content of nutrients in plant biomass, as well as an increase in total biomass, is noted. For example, Rosli et al [49] showed that the treatment of palm biochar together with hydroton led to maximum height, leaf area and total biomass of Latuca sativa grown hydroponically. A study by Mohsenzadeh et al [50] reported a more effective effect of biochar combined with humic acids compared to standard hydroponic fertilizer on biomass and fruit number of strawberries.

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3.3 Some potential of Ahnfeltia biochar application

Each type of biochar may have different effects depending on the application conditions and therefore should be tested under application conditions [30].

Luvic Anthrosols in Primorsky Krai have problems associated with low pH (acidic soils), heavy mechanical composition and soil overmoistening. Overmoistening of soils is caused on the one hand by mechanical composition, on the other by the monsoon climate of the region. The problems described for Luvic Anthrosols are risks for growing agricultural crops.

We previously studied wood biochar from Betula alba (78% C, pH 8.09, 110% water holding capacity in the natural fraction and 242% in the fraction <1 mm) on Luvic Anthrosols of Primorsky Territory for several years [51]. The application of biochar increased crop yields and reduced CO_2 flux from the soil. No significant changes were noted for particle size distribution, carbon content. An effect of biochar on soil pH was expected, but we did not note any significant changes.

Ahnfeltia biochar compared to biochar from Betula alba has a higher value of N, P and K, a significantly higher value of water-holding capacity. Thus, Ahnfeltia biochar can probably have a better effect on the properties of Luvic Anthrosols, as well as on soils with similar properties. For example, Umbisols showed an increase in pH and macronutrients when adding algal biochar [19]. For hydroponic systems, Ahnfeltia biochar can serve as a replacement for some imported fertilizers or as an addition to existing technologies.

There are no precise estimates of the amount of beach emissions in Primorsky Territory. However, up to 5000 tons of Ahnfeltia are annually emitted onto the beaches of Peter the Great Bay (part of the Primorsky Territory coast) alone [4]. According to calcultions, pyrolysis of wet Ahnfeltia at a temperature of 500 °C for 30 minutes produces about 42% biochar from the original biomass. Thus, 2100 tons of biochar can be obtained from 5000 tons of Ahnfeltia. With a biochar application rate of 10 t/ha of soil, 2100 tons of biochar is enough for 210 hectares.

For a small hydroponic setup with a 20-liter tank, 600 g of biochar is needed to maintain the P_2O_5 concentration in the aqueous solution at 20 mg/100 ml.

Thus, from a scientific point of view, the processing of Ahnfeltia into biochar can have the following positive effects: i) reduction of greenhouse gas emissions from beach soils during Ahnfeltia harvesting; ii) reduction of greenhouse gas emissions from agricultural soils; iii) long-term carbon sequestration; iv) improvement of soil quality; v) increase in crop yields, etc.

On the other hand, economic calculations of the full cycle of processing beach Ahnfeltia into biochar are needed, including an assessment of the consumer market and risks. Possible economic risks may include: i) the frequency and quantity of beach emissions; ii) a possible shortage of the product, for example, for the agricultural sector; iii) the readiness of the consumer market to use biochar; iv) the competitiveness of biochar on the local market, etc.

4. Conclusion

4.1. The use of Marine Macrophytes is Quite Promising for Obtaining Biochar

Medium-temperature Ahnfeltia biochar showed high agronomic characteristics. The pH of Ahnfeltia biochar was 8.0±0.5, organic carbon according to EDX was 83%, P_2O_5 was 365±12 mg/100 g, K_2O was 892±45 mg/100 g, water-holding capacity in the natural fraction was 432.5%. Ahnfeltia biochar is toxicologically safe.

Active storm events in Primorsky Krai provide stable beach emissions of Ahnfeltia, and only a small part of the coastline of the region contains up to 5 thousand tons of Ahnfeltia per year. Thus, using medium-temperature pyrolysis, it is possible to obtain up to 2100 tons of Ahnfeltia biochar annually. This amount of biochar is sufficient for application to 210 hectares of a field at an application rate of 10 t/ha. To ensure the required concentration in an aqueous solution of P_2O_5, it is necessary to add Ahnfeltia biochar at a dose of 3 g/l. Ahnfeltia biochar is promising for use both in soil and in nutrient solutions for hydroponics. The natural origin of biochars from marine macrophytes makes them suitable for organic agriculture. To estimate the cost of production of Ahnfeltia biochar, economic calculations are necessary, including transportation of raw materials, energy costs for pyrolysis, and production risks.

Our research is the initial stage for assessing Ahnfeltia biochar as an organic fertilizer.

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

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