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Baltic macroalgae as a potential source for commercial applications – review

Introduction

The Baltic Sea is a well-known shallow inland sea that lies on the continental shelf in northern Europe. The Baltic Sea separates the Scandinavian Peninsula from the rest of continental Europe and is surrounded by nine countries (i.e. Sweden, Finland, Russia, Estonia, Latvia, Lithuania, Poland, Germany, and Denmark). The Baltic Sea is an arm of the Atlantic Ocean, extending from northern Germany and Poland in the south almost to the Arctic Circle in the north. The area of the Baltic Sea, together with the Kattegat, covers about 415,000 km^2. The Baltic Sea is classified as one of the world's 66 "large marine ecosystems" (Snoeijs-Leijonmalm et al., 2017). The marine influence on the Baltic Sea ecosystem is large but it is strongly influenced by freshwater as well. The average salinity of the Baltic Sea is 7.5%, while the ocean's salinity is 36.6%. Salinity is also one of the main determinants of species diversity in macroalgae (Rybak, 2018). The flora of the Baltic Sea is relatively poor, which means that there are few plant species in the Baltic Sea (Deluga, 2018). However, despite the low salinity of Baltic waters, there is a group of organisms that creates an interesting ecosystem.

Algae are considered one of the first forms of life that demonstrated the ability to photosynthesize, and they appeared on Earth about one and a half billion years ago. These autotrophic non-tissue organisms are the most numerous group of self-nutrient aquatic organisms, and their growth is enabled by components such as phosphorus and nitrogen, as well as carbon dioxide and sunlight (Buchholz et al., 2012). They do not have vascular systems, leaves, stems, and roots, but only elements that resemble them (Bedoux et al., 2014). Macroalgae are rich in various biologically active substances valued for their unique properties. Currently, algae biomass is a renewable source with many active substances that are widely used the chemical, food, agriculture, cosmetics, pharmacy, and medicine industries, among others (McLachlan,

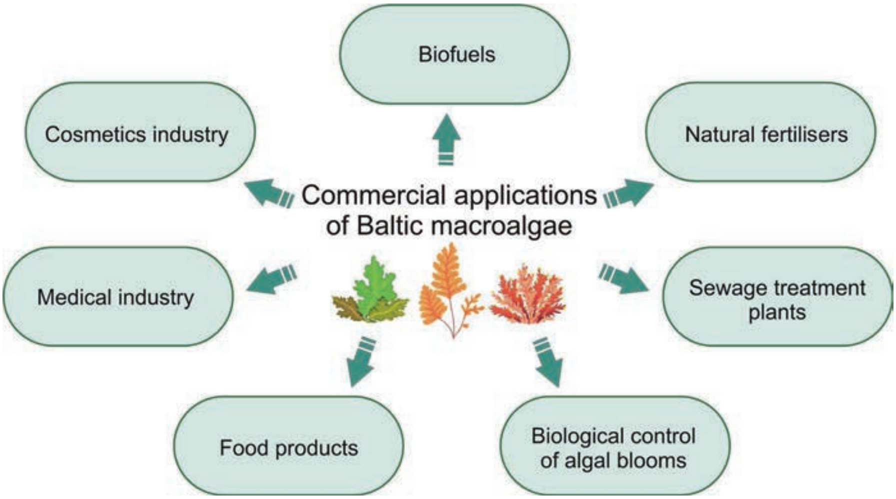

Fig. 1. Examples of the possible use of Baltic macroalgae as industrial resources

1985). An example of the commercial application of algae mass resources from the Polish part of the Baltic Sea is the use of *Furcellaria fastigiata* for agar production (Biłos et al., 2016). Moreover, in Poland, selected groups of macroalgae have been used as a raw material for industry and agriculture. This group of algae includes *Ulva* sp. and *Cladophora* sp., which most often form high biomass in freshwater reservoirs (Schroeder et al., 2013).

Macroalgae are classified as so-called: green algae (Chlorophyta Reichenbach, emend. Pascher, emend. Lewis & McCourt), brown algae (Phaeophyceae Kjellman) and red algae (Rhodophyta Thuret, emend. Rabenhorst, emend. Adl et al.). Macroalgae are a source of mineral substances, polysaccharides, proteins, lipids, phytohormones, and pigments, as well as many different secondary metabolites (phenolic compounds, terpenoids, halogenated compounds, sulfur derivatives, and nitrogen derivatives), and their biochemical composition depends on where the samples were taken, harvest season, and the environment (Buchholz et al., 2012). Hence, it is of important interest to present the possibilities for practical use of macroalgae derived from diverse ecosystems, such as the Baltic Sea (Fig. 1).

The potential use of bioactive compounds of Baltic macroalgae in the medical and cosmetic industry

Macroalgae abound in various active substances used in medicine and the cosmetic industry (Bedoux et al., 2014). Macroalgae are considered a source of bioactive compounds because they can produce many different secondary metabolites characterised by a broad spectrum of biological activity (Gupta, Abu-Ghannam, 2011).

Baltic macroalgae used in the cosmetic industry

The use of macroalgae in the cosmetic industry is becoming increasingly desirable due to the natural ingredients' broad spectrum and that they are easy to harvest, while at the same time they do not harm the environment. The biomass of marine macroalgae is often used to produce ingredients in cosmetics. These ingredients can have one of three main functions: as additives that contribute to organoleptic properties, to stabilise and preserve a product, or as bioactive compounds that perform the true function and cosmetic activity (Bedoux et al., 2014). It has been shown that metabolites derived from macroalgae are useful in many aspects of anti-aging, anti-cellulite, and slimming care, as well as having antioxidant, photoprotective, moisturizing, and whitening properties (Wang et al., 2014). The diversity of macroalgae species and their broad biochemical composition means that they are a potentially a source of bioactive compounds (Buchholz et al., 2012). Macroalgae are rich in vitamins such as A, B_1, B_2, B_3, B_5, B_6, B_9, B_{12}, C, D, E, and K, i.e. virtually all essential amino acids, macroelements and trace elements, such as iodine.

The skin aging process results from various factors inside and outside the body, which include diet, the passage of time and subsequent changes in the body, environmental pollution, and exposure to light or stress (Bedoux et al., 2014). During skin aging, cells lose the ability to regulate generated reactive oxygen species and suffer from oxidative stress. In the epidermis and dermis, the number of melanocytes and keratinocytes is reduced, as well as the ability to multiply cells and migrate fibroblasts, leading to a decrease in cellular activity and protein synthesis (Wang et al., 2014). Sulphated polysaccharides that are derived from marine algae may have various biological and biochemical effects, i.e. modulating proteolysis of connective tissue, anti-inflammatory effects, adversely affecting the development of free radicals and antioxidants, as well as prevention of oxidative damage. These properties, among others, have been identified for green algae, *Ulva lactuca* L. and *Codium tomentosum* Stackhouse (Bedoux et al., 2014). *Ulva* populations originated mainly from shores and estuaries, with a minor number occurring in ocean lagoons, coastal lakes, canals, and rivers. *Ulva* species were present in a very wide range of saline waters (from fresh to hypersaline waters) (Rybak, 2018). Therefore, the genus *Ulva* is common in the Baltic Sea and may constitute 22–75% of biomass in the Gulf of Gdańsk (Filipkowska et al., 2009). It is also worth mentioning that *U. lactuca* is one of the macroalga from the Baltic Sea described by Linnaeus (Dominguez, Loret, 2019) and an organism that can be efficiently used in the cosmetic industry. Additionally, other species of *Ulva* occur in the Baltic Sea – *U. flexuosa* Wulfen, *U. intestinalis* L., and *U. linza* L., whose potential health properties have not yet been studied (Fig. 2). On the other hand, *Codium tomentosum* is not a typical species

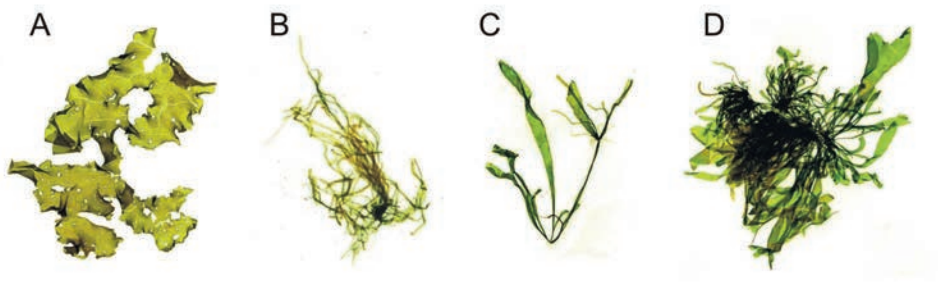

Fig. 2. Different *Ulva* species that occur in the Baltic Sea: *Ulva lactuca* L. (A), *Ulva flexuosa* Wulfen (B), *Ulva intestinalis* L. (C), and *U. linza* L. (D) (Photo. S. Śliwińska-Wilczewska)

found in the Baltic Sea. However, the other species, *C. fragile,* can be found in the Kattegat (Nyberg, 2007).

Macroalgae are also an important source of amino acids, amino acid derivatives and peptides which can stimulate collagen production in the human skin. Additionally, hydrolysates of algae proteins from macroalgae of the genus *Undaria*, *Sargassum*, *Porphyra*, *Palmaria*, and *Ulva* show antioxidant activity, which is important in anti-aging care. These species: *Sargassum muticum* (Yendo) Fensholt, *Porphyra umbilicalis* Kützing, *Palmaria palmata* L., and *Ulva* sp., also occur in the Baltic Sea (Snoeijs-Leijonmalm et al., 2017). It is worth noting that many marine macroalgae cannot survive the low salinity of the Baltic Sea; however, these species are still found in the lower sublittoral of the Belt Sea (*HELCOM*, 2012; Snoeijs-Leijonmalm et al., 2017). Furthermore, a polypeptide from *Ulva* sp., called Aosa biopeptide, is used in cosmetic products and consists of glycine, arginine, lysine, valine, and aspartic acid. The tripeptide consisting of arginine-glycine-aspartic acid was found to stimulate mechanisms underlying collagen production through tissue growth factor and cause an increase in collagen biosynthesis in human fibroblasts. Biopeptides from macroalgae can be used as a potential source of synthetic components and can contribute to the prevention of aging. Enzymatic hydrolysis of algae proteins could allow for the isolation of peptides useful in the development of skin bioactive compounds. External aging causes exposure to UV radiation and associated irritation, characterized by a deterioration of the extracellular skin matrix and keratinocyte dysplasia in the epidermis, causing wrinkles, flabbiness, roughness, and spotty pigmentation. UV light is divided into UVA, UVB, and UVC. UVA can penetrate the dermis and not only causes wrinkles but also various skin-related ailments; UVB is more carcinogenic and causes the skin to turn red and burn 1,000 times faster than UVA; while UVC is blocked by the ozone layer, and therefore does not pose a risk to the skin (Wells et al., 2017). Macroalgae have mechanisms that counteract the harmful effects of UVB and UVA, producing photosynthetic pigments such as carotenoids and phenolic compounds (e.g. phlorotannins) or compounds that absorb UV radiation. UV absorbing compounds are bioactive and can protect human fibroblast cells against cell death caused by UV radiation and inhibit the aging of human skin (Bedoux et al., 2014).

Moisturizing is the most important step in preventing skin aging by helping to maintain a healthy appearance and elasticity while strengthening its protective barrier against harmful environmental factors. Polysaccharides derived from macroalgae are environmentally friendly substances, relatively inexpensive, and can be used as substitutes for petrochemical products. Polysaccharides and oligosaccharides provide a high water storage capacity. Macroalgae extracts contain floridoside and isofloridoside acids. These components have properties that enable them to increase water retention in the stratum corneum, and thus take part in moisturizing the skin. It was noted that the red algae *Chondrus crispus* (L.) J.Stackhouse are rich in polysaccharides and minerals that have a moisturizing, firming, and soothing effect. Moreover, extract from the green algae *Codium* sp. can regulate the distribution of water in the skin, and thus protect the skin from dryness, especially in an arid environment (Wells et al., 2017). The described macroalgae species (*Chondrus crispus* and *Codium fragile* (Suringar) Hariot) can be found in the west area of the Baltic Sea (Snoeijs-Leijonmalm et al., 2017). *C. crispus* and *C. fragile* live permanently submerged in the Kattegat at a water depth that ranges from 0.5–1 m to 4–5 m (Nyberg, 2007).

Cellulite is a cosmetic problem that causes the appearance of hollows on the skin surface. This problem is a combination of expanding fat cells that accumulate under the skin and fibrous stripes that run perpendicular to the skin's surface. Cellulite includes changes in the biochemistry of the subcutaneous fat layer. These changes include increased lipogenesis, reduced lipolysis, and increased lipid storage in fat cells. Energy homeostasis is regulated by the chronobiology of fat cells through the mechanisms of lipogenesis and lipolysis. Some local cellulite treatments include macroalgae extracts, such as those used to increase microcirculation flow, reduce lipogenesis, and improve lipolysis, which restore the normal structure of the dermis and subcutaneous tissue and remove or prevent free radicals. The macroalgae most commonly used in anti-cellulite and slimming preparations are brown algae, *Fucus vesiculosus* L., *Furcellaria lumbricalis* (Hudson) J.V.Lamouroux, *Laminaria digitata* (Hudson) J.V.Lamouroux, and *Pelvetia* sp. (Bedoux et al., 2014). They stimulate blood flow and help the body excrete excess fluid. Thus, the Baltic macroalgae *Fucus vesiculosus* and *Furcellaria lumbricalis* can reduce or eliminate cellulite problems (Fig. 3).

The potential use of macroalgae in the medical industry

Macroalgae are also becoming increasingly popular due to properties that are useful in the medical industry (Buchholz et al., 2012). The most bioactive compounds in mac-

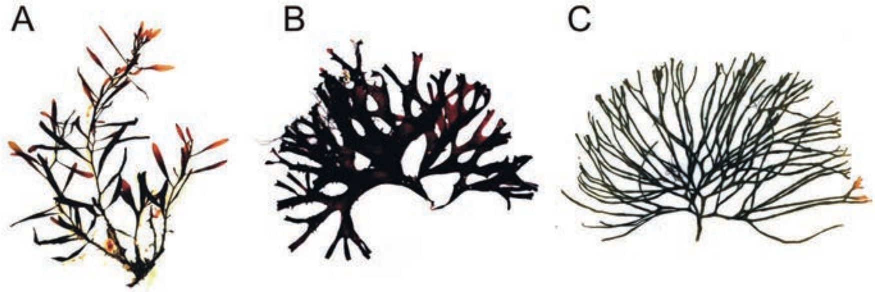

Fig. 3. Examples of the Baltic macroalgae: brown algae *Sargassum muticum* (Yendo) Fensholt (A), red algae *Chondrus crispus* L. (B), and green algae *Codium fragile* (Suringar) Hariot (C) that can be used in the cosmetic industry (Photo. S. Śliwińska-Wilczewska)

roalgae include sulfated polysaccharides, phlorotannins, and diterpenes. These compounds have strong antiviral, antibacterial, and anticancer properties. Polysaccharides are a class of macromolecules that are increasingly gaining importance in the field of biochemistry and medicine due to their immunomodulatory, anticancer, antiviral, and antithrombotic effects. They are mainly present in cell walls and their composition varies depending on the season, age, species, and geographical location of the macroalgae (Gupta, Abu-Ghannam, 2011). In addition to confirmed anticoagulant and antiviral activity, they act on the inflammatory and immune systems. Macroalgae produce various polysaccharides, such as alginic acid (also called algin), fucoidan, and laminarin (also known as laminaran) (Milledge et al., 2015). Alginate produced by brown algae, especially in the form of sodium and calcium alginate, is widely used in the pharmaceutical industry due to its ability to chelate metal ions and create very sticky solutions, while sulfated polysaccharides from macroalgae show various biological activities with potential medical value, including antitumor, antiviral, and antioxidant activity.

Fucoxanthin is another interesting compound. Fucoxanthin is the main biofunctional pigment present in brown algae and is one of the most numerous carotenoids found in nature. Fucoxanthin has antioxidant and anti-cancer properties. It has recently been found that fucoxanthin can help increase metabolism, thereby controlling weight gain (Gupta, Abu-Ghannam, 2011). There are many different species of brown algae in the Baltic Sea, including species of the genus *Fucus* (*Fucus cottonii* M. J. Wynne & Magne, *F. evanescens* C. Agardh, *F. radicans* L. Bergström & L. Kautsky, *F. serratus* Thunberg, *F. spiralis* L., *F. vesiculosus*), as well as *Ascophyllum nodosum* L., *Ectocarpus siliculosus* (Dillwyn) Lyngbye, *Scytosiphon lomentaria* (Lyngbye) Link, *Chorda filum* L. and *Pylaiella littoralis* L., hence, Baltic brown algae could useful to both the pharmaceutical and the medical industries (Snoeijs-Leijonmalm et al., 2017).

Baltic macroalgae used in the food industry

Macroalgae, due to their richness in vitamins and macroelements, are often use in the food industry. From a nutritional point of view, edible macroalgae are low-calorie foods with a high concentration of minerals, vitamins, and proteins, and low lipid content. Currently, they are willingly consumed on a global scale. Thanks to their interesting properties, they are also used in the production and processing of food products such as emulsifying, gelling, or water-retaining agents. Macroalgae are an excellent source of vitamins A, C, D, and E and group B vitamins such as ribose, niacin, pantothenic acid, and folic acid (Fitzgerald et al., 2011). They also derive an unusual wealth of minerals from the sea, which can constitute up to 36% of their dry matter. Macronutrients include sodium, calcium, magnesium, potassium, chlorine, sulfur, and phosphorus as well as micronutrients such as iodine, iron, zinc, copper, selenium, molybdenum, fluorine, manganese, boron, nickel, and cobalt (Kandale et al., 2011). It follows that the composition of macroalgae comprises almost all of the vitamins, the most important macroelements necessary for the proper functioning of the human body, as well as iodine which is responsible for a healthy thyroid (Buchholz et al., 2012). As a result, algae are often used as components of a healthy diet, in the form of salads, soups, various types of snacks, and also as widely distributed dietary supplements in well-developed countries to help maintain health.

Macroalgae are a rich source of iodine. The highest iodine content is found in brown algae. In most cases, red and green algae have lower iodine content but still a high value compared to terrestrial plants. The daily adult requirement for iodine is currently 150 μg per day, and this dose can be reached by very small amounts of macroalgae. Just one gram of dried brown algae contains 500 to 8,000 μg of iodine, and green algae and red algae provide 100–300 μg in one gram (Kandale et al., 2011). It follows that the introduction of a small number of macroalgae into the diet is enough to maintain a healthy thyroid. Furthermore, a large part of the world population receives insufficient iodine because other food sources (plants, animals) contain very low levels of this element.

An interesting feature of macroalgae is their richness of proteins and bioactive peptides. The composition and concentration of proteins depend on the species, place, and time of harvest. The protein fraction of brown algae is relatively low (1–24% of dry matter) compared to green algae (4–44% of dry matter) and red algae (5–50% of dry matter) (Fitzgerald et al., 2011). Most macroalgae contain all necessary amino acids and acidic amino acids, e.g. glutamic and aspartic acids, and as is well known, protein is a critical nutrient due to its very important role in the human body. Macroalgae are a very good source of nutrients and have a relatively low-fat content (0.3–5% of dry matter) (Bedoux et al., 2014).

Macroalgae also contain large amounts of polysaccharides (which include hydrocolloids), especially in their cell walls. Hydrocolloids have gained commercial significance as food additives. The food industry uses their gelling, water-retaining, emulsifying, and other physical properties. Agar is used in food products such as confectionery, meat and poultry products, desserts and drinks, and molded foods. Carrageenan is used in salad and sauces, dietary foods, and as a preservative in meat and fish products, dairy products, and baked goods (Kandale et al., 2011). Regular consumption of macroalgae has many positive health benefits which were describe in the previous chapter. Macroalgae are also widely used in the food industry as thickening aqueous solutions, for gel production, and in the production of items such as toothpaste, ice cream, and anti-cancer mayonnaise (Milledge et al., 2015).

Macroalgae have gained great popularity as an interesting addition to dishes or as basic ingredients of dishes. The best example is sushi, which is a well–known food across the world, for which nori (red algae *Porphyra umbilicalis*) is needed. Other examples are Kombu (brown algae *Laminaria japonica* Areschoug) and Wakame (brown algae *Undaria pinnatifida* (Harvey) Suringar), which are used in various types of salads, soups, and starters (Kolb et al., 2004). Although the mentioned species do not occur in the Baltic Sea, other common Baltic species of brown algae (e.g. *Fucus* sp., *Ascophyllum* sp.) or red algae (e.g. *Furcellaria* sp., *Polysiphonia* sp.) can be successfully used in the food industry.

Possible use of Baltic macroalgae in the energy industry

The energy industry is of vital importance for the proper functioning of the world's economies. Alternative energy sources are being sought out as non-renewable resources are becoming depleted. Carbon, which is the most basic energy source in Poland, is not an ideal source of energy due to the negative impact on the environment during its combustion or extraction, similar to oil. Therefore, alternative raw materials are sought, with one being biodiesel obtained from macroalgae. For now, it is quite a promising material that has great market potential, as its production can be very profitable with low environmental losses. At present, macroalgae are not widely used as energy sources; however, many promising studies are being conducted in this direction (Filipkowska et al., 2008).

Several solutions have been proposed for the production of biofuels to replace fossil fuels. Biodiesel and bioethanol produced by terrestrial plants have attracted the world's attention as potential alternative solutions. However, due to the other various uses of terrestrial plants, e.g. for consumption, doubts have arisen about converting them to biofuels. Therefore, it is necessary to find a new raw material for the production of biofuels that can generate similar by-products as terrestrial plants but can be produced solely for energy purposes. Macroalgae are one alternative to conventional terrestrial plant cultivation. The production of biofuels from macroalgae is widely considered to be one of the most suitable methods. These plants are an economically and environmentally sustainable renewable biomass source for biofuel production because they are simple aquatic organisms that carry out photosynthesis and their diversity is much greater than terrestrial plants. Almost all of macroalgae biomass can be converted into energy and their waste residues into methane and hydrogen. They also contain oils that can be used as a raw material for biodiesel and carbohydrates that can be converted into bioethanol. Macroalgae have the advantage of not interfering with food production and have the potential to cover global demand for transport fuels (Suganya et al., 2016).

Anaerobic digestion is a biological process used to produce methane-rich gas from biomass. This digestion process involves the following steps: *i*) hydrolysis of organic matter, *ii*) the synthesis of acetic acid from hydrolysis products, and *iii*) the production of methane by the relevant bacteria. Macroalgae have a similar composition as other sources of organic materials and should be adapted to existing anaerobic digestion installations. However, the content of seaweed-related compounds, such as salts, can inhibit the fermentation process. Therefore, they need to be pre-processed, including at minimum washing, to prevent inhibition of the fermentation process (Milledge et al., 2014). Anaerobic fermentation of macroalgae allows for the production of biogas consisting of about 60% methane and 40% CO_2 (and trace amounts of CO, H_2S, H_2, N_2, and O_2). The composition of macroalgae may also vary depending on the season and location, which may affect production performance. For example, the methane yield of *Saccharina latissima* (Linnaeus) C.E.Lane (syn. *Laminaria saccharina* (L.) Lamouroux) algae is twice as high from material collected in autumn than material collected in spring (Roesijadi et al., 2010). *S. latissima* occurs in the west area of the Baltic Sea; however, this species is poorly adapted to the low salinity. It is assumed that at the inner Baltic distributional limit of *S. latissima* in the southern Baltic Sea proper, its upper limit lies at the water depth of about 20 m (Wærn, 1965). Fermentation of biomass to ethanol consists of two reactions: *i*) hydrolysis of organic material to simple sugars (using high temperature, enzymes, or acids) and *ii*) fermentation of sugars to ethanol. Macroalgae use polysaccharides such as sulfated polysaccharides, mannitol, alginates, agar, and carrageenan to produce ethanol. Brown algae, especially those of the genus *Laminaria*, are the most desirable macroalgae for alcoholic fermentation because they contain the most polysaccharides. Macroalgae biomass has great potential for producing biofuels, although there are challenges in its processing. However, much research is currently underway to identify methods for maximizing its potential for energy generation (Milledge et al., 2014).

Baltic macroalgae as natural fertilisers and products for wastewater treatment

Macroalgae are becoming increasingly popular as natural fertilisers. This is due to the presence of nitrogen, magnesium, potassium, and some trace elements in their composition (Mohy El Din, 2015). These plants also have a great ability to absorb nitrogen and phosphorus, which are very important to their growth. In addition to macroelements and microelements, they also contain phytohormones, which positively affect growth of macroalgae. Liquid macroalgae extracts and suspensions have gained wider application than microalgae meal due to their ease of use. Most often, fertilisers are based on algae such as *Ascophyllum* sp. and *Fucus* sp. These macroalgae are found mainly in the western part of the Baltic Sea. The intertidal species *F. vesiculosus* lives permanently submerged in the Kattegat. It grows just below the water surface, with *F. spiralis* above it and *Ascophyllum nodosum* (Linnaeus) Le Jolis and *Fucus serratus* L. below it (Snoeijs-Leijonmalm et al., 2017). Large amounts of insoluble carbohydrates act as soil improvers (better aeration, structure) and also help retain soil moisture. It has been shown that they not only provide nutrients needed for growth but also increase seed germination, improve tolerance to low temperatures, and are harmful to some insects (Milledge et al., 2015). They can, therefore, be an alternative to abused chemical fertilisers that have a negative impact on the environment

There are two main areas where macroalgae have the potential to be used in wastewater treatment. The first is for wastewater and some agricultural waste treatments to reduce total nitrogen- and phosphorus-containing compounds before release of these purified waters into rivers or oceans. The second is for the removal of toxic metals from industrial wastewater. Macroalgae can be used to reduce nitrogen and phosphorus content in wastewater after treatment. Many microalgae take up ammonium as an absorbable form of nitrogen for growth, and this ion is a common form of nitrogen in most domestic and agricultural wastewater. Another important feature of many macroalgae is their ability to absorb large amounts of phosphorus (McHugh, 2003). The usefulness of macroalgae in wastewater treatment is increasingly known but its large-scale application has not yet been implemented, although this may change with growing awareness of the need to protect the marine environment. The accumulation of heavy metals such as copper, nickel, lead, zinc, and cadmium by macroalgae became apparent when they were consumed and their chemical composition studied. The content of heavy metals, especially in large brown algae, depends on their geographical location as well as their proximity to industrial points. For this reason, the idea of using macroalgae as biological indicators of heavy metal pollution, both from natural sources and from activities such as the extraction or disposal of industrial waste, was proposed (McHugh, 2003; Żbikowski et al., 2006, 2007). Removal of toxic metals was implemented using brown algae of the genera *Sargassum*, *Laminaria* and *Ecklonia* and the green algae *Ulva* sp. They were also used to remove heavy metals in wastewater treatment (McHugh, 2003). Among these organisms, *Sargassum muticum* occurs in the Baltic Sea but only in the more saline areas in the Arkona Sea, the Belt Sea, and the Öresund (Nyberg, 2007). *Ulva* sp. is commonly found in the entire Baltic Sea. It is possible to use Baltic macroalgae to remove heavy metals near factories, processing plants, and sewage treatment plants as one of the stages in this process.

Macroalgae as a biological factor limiting the occurrence of massive cyanobacterial blooms in the coastal area of the Baltic Sea

The presence of macroalgae is of great importance for the biological structure, ecosystem functioning, and water quality in shallow water bodies (van Donk, van de Bund, 2002; Hilt, Gross, 2008), as well as in the Baltic Sea. Underwater meadows provide shelter for the development of numerous animals and are the basis of the diet for aquatic organisms (Rybak, 2016; Wells et al., 2017). They can also be used to assess the ecological state of the marine environment (Saniewski, 2013). Macroalgae effectively compete with phytoplankton species for available nutrients (Rybak, Gąbka, 2018). It has been shown that in a large number of cases, allelopathic compounds produced by macroalgae act on organisms in a different way than most synthetic herbicides (Ohad, Hirschberg, 1990; Huppatz, 1996). These compounds have a broader range of action on target organisms than synthetic inhibitors (Duke et al., 2001). Therefore, the importance of the allelopathic effects of macroalgae in aquatic ecosystems is gaining interest due to their potential ability to control or limit the occurrence of organisms forming massive blooms, including harmful cyanobacteria (Berger, Schagerl, 2003; Wang et al., 2007; Tang, Gobler, 2011; Pakdel et al., 2013; Ghobrial et al., 2015).

Złoch et al. (2018) tested the allelopathic activity of several representatives of Baltic macroalgae from the genus *Chara* on the growth of picocyanobacteria *Synechococcus* sp. It was shown that the addition of aqueous extracts from *Chara aspera* C.L.Willdenow, *C. baltica* (C.J.Hartmann) Bruzelius, and *C. canescens* Loiseleur significantly affected the cell number in *Synechococcus* sp. culture. The addition of aqueous extracts from *C. canescens* in a concentration of 5, 25, and 50 $\mu L\ mL^{-1}$ caused the cell number of picocyanobacteria to decrease to 86%, 78%, and 48%, respectively, after a week of exposure, compared to control conditions. On the other hand, the addition of 25 and 50 $\mu L\ mL^{-1}$ extracts obtained from *C. baltica* caused a reduction in the cell number of *Synechococcus* sp. to 55% and 44%, respectively. In turn, the addition of 50 $\mu L\ mL^{-1}$ of an extract from *Chara aspera* inhibited the growth of picocyanobacteria after a week of exposure. In this experiment, the number of picocyanobacteria cells decreased to 90% compared to the control treatment. It is believed that the chemical composition and proportions of allelopathic compounds may play a significant role in determining their effect on the growth of various phytoplankton species, including cyanobacteria (Pakdel et al., 2013). Therefore, weaker inhibition of the growth of picocyanobacteria by *C. aspera* extract, compared to *C. baltica* and *C. canescens*, may be due to the presence of various allelopathic compounds and their concentrations. This varied sensitivity to allelopathic compounds indicated that species belonging to the genus *Chara* may affect the growth and occurrence of *Synechococcus* sp. Moreover, the negative effects may be stronger in the natural environment, since these macroalgae occupy large areas of the bottom of the southern Baltic Sea and allelopathic compounds can be constantly released into environment (Granéli, Hansen, 2006). Studies demonstrating the allelopathic activity of *C. aspera*, *C. baltica*, and *C. canescens* on *Synechococcus* sp. indicated that these macroalgae may potentially control the extent of picocyanobacteria in coastal Baltic waters.

As mentioned earlier, the lack of recognition of the allelopathic activity of Baltic macroalgae from the southern Baltic region on the associated species of filamentous cyanobacteria prompted us to conduct relevant laboratory experiments. Representatives of typical the Baltic macroalgae *Ulva intestinalis*, as well as filamentous cyanobacteria *Nodularia spumigena* and *Nostoc* sp., were selected for the study. The cyanobacteria strains were maintained as a non-axenic batch culture in the Culture Collection of Baltic Algae (CCBA) at the Laboratory of Marine Plant Ecophysiology, University of Gdańsk, Poland. The brackish macroalga was selected, based on the allelopathic potential of species from the order of *Ulvales* (e.g. Wang et al., 2007).

Baltic *U. intestinalis* was collected manually from the coastal zone of the Gulf of Gdańsk, Poland (54°47′13.8″N 18°25′33.7″E) and carefully washed several times with distilled water in the laboratory to remove attached organisms as described by previous researchers (Złoch et al., 2018). The allelopathic effects of *U. intestinalis* were tested according to a method proposed by Wang et al. (2007) with modifications. The monocultures of cyanobacteria *Nodularia spumigena* Mertens ex Bornet & Flahault and *Nostoc* sp. were exposed to three concentrations of both water extracts and filtrate originating from *U. intestinalis*. The final concentrations of extract and filtrate were: 5, 25 and 50 μL mL^{-1}. Moreover, to compare the effects on the two cyanobacteria of different concentrations of fresh tissue from the *U. intestinalis*, coexistence assays were performed using a mixed culture system of one macroalga and one cyanobacteria. Different initial inoculation concentrations (0, 0.5, 2.5, and 5 g-wet wt L^{-1}) of fresh macroalgal tissues were inoculated into 25 mL Erlenmeyer flasks containing 20 mL f/2 culture medium. Selection of these concentrations was based on preliminary experiments to determine the most relevant effectiveness. It was found that the growth of target cyanobacterium *N. spumigena*, after addition of 5, 25, and 50 μL mL^{-1} filtrate and the presence of 0.5, 2.5, and 5 g-wet wt L^{-1} live tis-

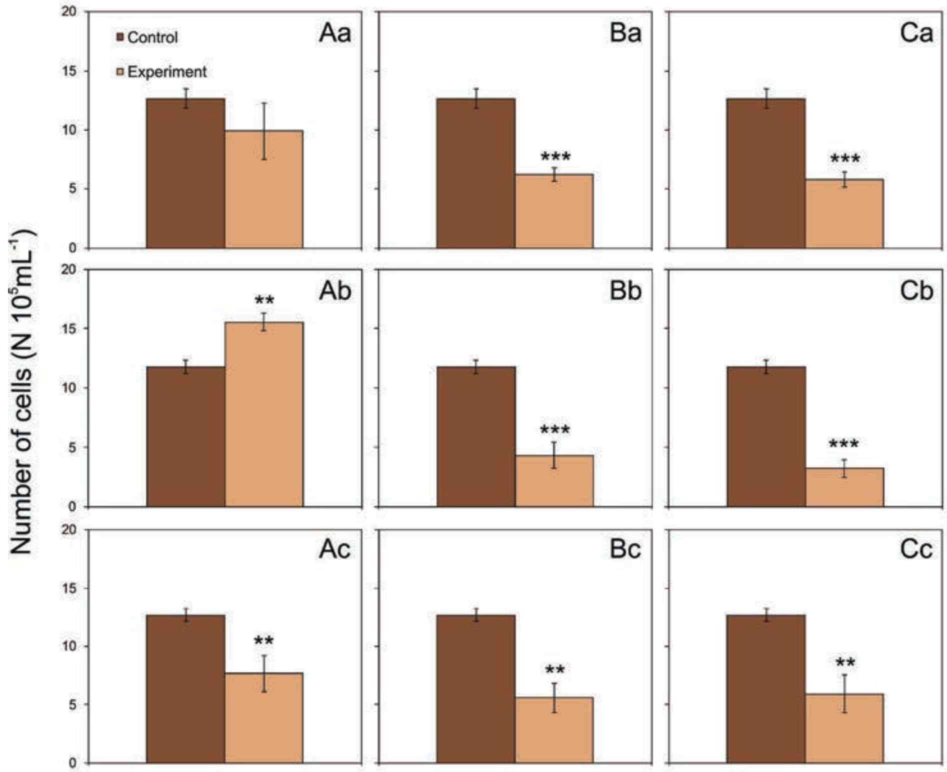

Fig. 4. The number of *Nodularia spumigena* Mertens ex Bornet & Flahault cells (10^5 cell mL^{-1}) for controls and experiments with addition of (A) extracts: 5 (a), 25 (b), and 50 (c) (μL mL^{-1}), (B) filtrate: 5 (a), 25 (b), and 50 (c) (μL mL^{-1}), and (C) tissue: 0.5 (a), 2.5 (b), and 5 (c) (g-wet wt L^{-1}) obtained from *Ulva intestinalis* L. after 14 days of exposure. The values refer to means (n = 3, mean ± SD). Asterisks indicate statistically significant difference compared to the control obtained with the ANOVA. Levels of significance were *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$.

sue from *U. intestinalis*, was significantly reduced to approximately 40%, compared to the control treatment (Fig. 4). On the other hand, the addition of filtrate and the presence of live tissue of *U. intestinalis* had no statistical effect on the number of *Nostoc* sp. cells ($p > 0.05$; Fig. 5).

Slight stimulation of the tested cyanobacteria was noted after the addition of aqueous extract, which may be the result of hormesis or the accumulation of nutrients in macroalgae tissue. Based on the results, it can be concluded that Baltic macroalgae of the genus *Ulva* have the potential to affect the occurrence and abundance of some bloom-forming species of cyanobacteria. Research on the allelopathic effect of macroalgae on the growth of filamentous and bloom-forming cyanobacteria occurring in the southern Baltic Sea region is an interesting pursuit that should be recognized as requiring continuation.

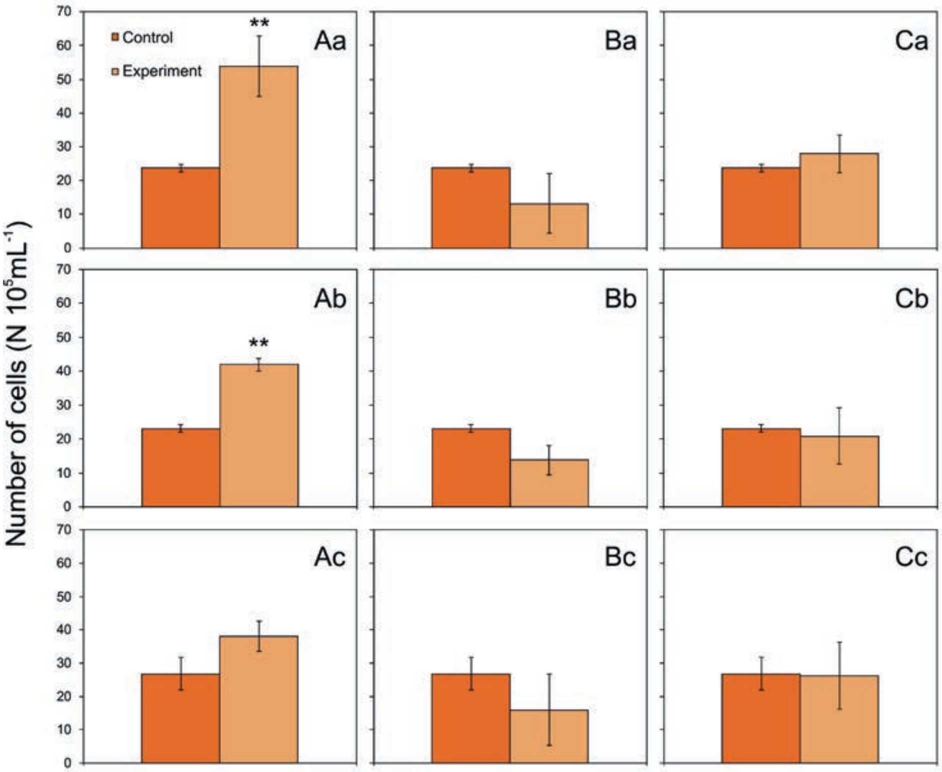

Fig. 5. The number of *Nostoc* sp. cells (10^5 cell mL^{-1}) for controls and experiments with addition of (A) extracts: 5 (a), 25 (b), and 50 (c) (µL mL^{-1}), (B) filtrate: 5 (a), 25 (b), and 50 (c) (µL mL^{-1}), and (C) tissue: 0.5 (a), 2.5 (b), and 5 (c) (g-wet wt L^{-1}) obtained from *Ulva intestinalis* L. after 14 days of exposure. The values refer to means (n = 3, mean ± SD). Asterisks indicate statistically significant difference compared to the control obtained with the ANOVA. Levels of significance were *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$.

Conclusions

Baltic macroalgae are organisms which may be used as industrial resources thanks to their unique properties. Due to their content of vitamins, as well as macro- and microelements, they are becoming increasingly popular as foods and supplements but also have great potential to gain significance in the pharmaceutical industry. Similar trends can also be observed in the cosmetic industry, where macroalgae are an increasingly important ingredient in anti-aging, anti-cellulite, and moisturizing products. The energy industry has also become interested in macroalgae due to the search for natural solutions for energy production, i.e. biofuel. Baltic macroalgae can also be used as natural fertilisers and products for wastewater treatment. Finally, based on the research, it can be concluded that some Baltic macroalgae may allelopathically affect bloom-forming cyanobacteria. Thus, the study of the allelopathic activity of macroalgae may help determine their possible role as an important biological factor affecting cyanobacterial blooms. Our review shows that the most economically important macroalgae species are found in the western part of the Baltic Sea. This is due to the greatest richness and variety of species.

Although it is worth noting that cosmopolitan species, such as *Ulva*, occur throughout the Baltic Sea, so in every region of this sea it is possible to utilize these organisms for commercial purposes. Thus, in our opinion, there are sufficient species resources in the waters of the Polish part of the Baltic Sea for commercial use. The question that arises is whether the degree of pollution of the Baltic Sea waters allows for the use of registered algae for cosmetic, pharmaceutical, and food purposes. Unfortunately, the current literature does not provide unambiguous answers to this question. Lack of sufficient data on the amount of accumulated heavy metals and other anthropogenic pollutants in macroalgae tissues and the specific limits that must be met leave this question open. The authors can only speculate that the use of algae that come from open water near the Danish straits, where the amount of pollution is less due to greater water exchange, is more favourable. Studies on the practical use of Baltic macroalgae are still ongoing. The results of previous studies are quite promising because Baltic macroalgae are easy to grow, relatively inexpensive, and less invasive, and these features are highly desirable in order to protect the environment and natural resources.

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Conflict of interest

The authors declare no conflict of interest related to this article.

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Bałtyckie makroglony jako potencjalne źródło zastosowań komercyjnych

Streszczenie

Morze Bałtyckie jest wyjątkowym ekosystemem wodnym, charakteryzującym się wyraźnymi zmianami w środowisku, szczególnie w odniesieniu do zasolenia i klimatu. Jest to także miejsce występowania morskich i słodkowodnych organizmów roślinnych, które od stuleci fascynują naukowców. Niewiele jest jednak prac prezentujących bałtyckie glony makroskopowe, jako potencjalne źródło dla zastosowań komercyjnych. Celem niniejszego opracowania było przedstawienie bałtyckich makroglonów, jako źródła zasobów przemysłowych. W przeglądzie uwzględniono, m.in. potencjał wykorzystania tych organizmów w przemyśle kosmetycznym i medycznym, w tym najważniejsze składniki, które czynią je cennym produktem spożywczym. Zwrócono także uwagę na ich rosnącą popularność i potencjalne wykorzystanie w przyszłości, np. jako biopaliwa, nawozy naturalne lub składniki oczyszczalni ścieków. Przedstawiono także możliwość wykorzystania makroglonów jako biologicznego czynnika, ograniczającego występowanie masowych zakwitów sinic w Morzu Bałtyckim.

Key words: Baltic macroalgae, Baltic Sea, bioactive compounds, biomass, industrial resources

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