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Global potential of offshore and shallow waters macroalgal biorefineries to provide for food, chemicals and energy: feasibility and sustainability

Yoav Lehahn [a], Kapilkumar Nivrutti Ingle [b], Alexander Golberg [b,*]

[a] Department of Earth and Planetary Sciences, Weizmann Institute of Science, Israel
[b] The Porter School of Environmental Studies, Tel Aviv University, Israel

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ABSTRACT

Displacing fossil fuels with renewables and increasing sustainable food and chemicals production are among the major challenges facing the world in the coming decades. Integrating climatological oceanographic data with a metabolism and growth rate model of the green marine macroalga from *Ulva* genus, we analyze the potential of offshore biorefineries to provide for biomass, ethanol, butanol, acetone, methane and protein, globally and in 13 newly defined offshore provinces. We show that for optimum fresh weight stocking density of 4 kg m^{-2} the total potential of offshore cultivated *Ulva* biomass is of the order of 10^{11} dry weight (DW) ton $year^{-1}$, over a surface area of ~10^8 km^2. We found that the distance of the offshore cultivation site to the processing facility is limited to 114–689 km, depending on cargo moisture content. The near-future technologically deployable areas, associated with up to 100 m water installation depth, and 400 km distance from the shore, can provide for 10^9 DW ton $year^{-1}$, which is equivalent to ~18 EJ. This has the potential to displace entirely the use of fossil fuels in the transportation sector or provide for 5–24% of predicted plant proteins demand in 2054. In addition, we modeled the potential production of ethanol, butanol, acetone and methane from the offshore produced biomass. Finally, we analyzed the environmental risks and benefits of large-scale offshore macroalgal cultivation. These results are important as they show for the first time the potential of offshore biomass cultivation to reduce the use fossil fuels and arable land to provide for food, chemicals and fuels required for the society.

1. Introduction

Global population growth and increase in quality of life in the era of changing climate will increase the demand for food, chemicals, and fuels. A possible, sustainable direction for addressing this challenge is the production of biomass and the conversion of this biomass to the required products through a complex system coined biorefinery. However, concerns over net energy balance, potable water use, environmental hazards, and uncertainty in the processing technologies — mostly the problems with lignin — raise questions regarding the actual potential of terrestrial biomass to meet the anticipated food, feed, and energy challenges in a sustainable way [1,2]. Alternative sources for biorefineries are offshore grown macroalgae (Fig. 1). Macroalgae have been harvested throughout the world as a food source and as a commodity for the production of hydrocolloids for centuries. However, to date macroalgae still present only a tiny percent of the global biomass supply of ~$17 \cdot 10^6$ fresh weight (FW) ton of macroalgae in comparison to $16 \cdot 10^{11}$ tons of terrestrial crops, grasses and forests [3–5]. A recent expanding body of evidence suggests that off-shore cultivated macroalgae, which contain very little lignin and do not compete with food crops for arable land or potable water, can provide an alternative source of biomass for sustainable production of food, chemicals, and fuels [3,6,7].

Different from macroalgae that still occupy a small niche of bioenergy and commodity chemicals in research and industry, microalgae has gained attention in the last decades as biofuel feedstock due to their high biomass yield per hectare [10]. However, the real scale implementation of microalgae systems for bioenergy and commodity chemicals production is limited today by costs associated with reactor construction and maintenance, contamination, and energy required for separation of these single cell organisms from water [12]. In a parallel vein, in the recent years, macroalgae have been considered a "third or even fourth generation" biofuel feedstock [13]. Currently, the macroalgae cultivation industry is mainly concentrated in Asia [11]. The major applications of macroalgae biomass today are food hydrocolloids.

There are several properties of macroalgae, which make them attractive feedstock for food ingredients, biofuels and industrial chemicals. First, macroalgae grow faster than terrestrial plants [14–16]. Second, macroalgae do not occupy arable land and do not consume fresh water [17], thus they do not compete with traditional food agriculture [13,18]. Third, macroalgae normally contain no or less lignin, eliminating the energy intensive lignin removal step in pre-treatment processes [6,19,20]. In comparison with microalgae, macroalgae derived

* Corresponding author.
E-mail address: agolberg@tauex.tau.ac.il (A. Golberg).

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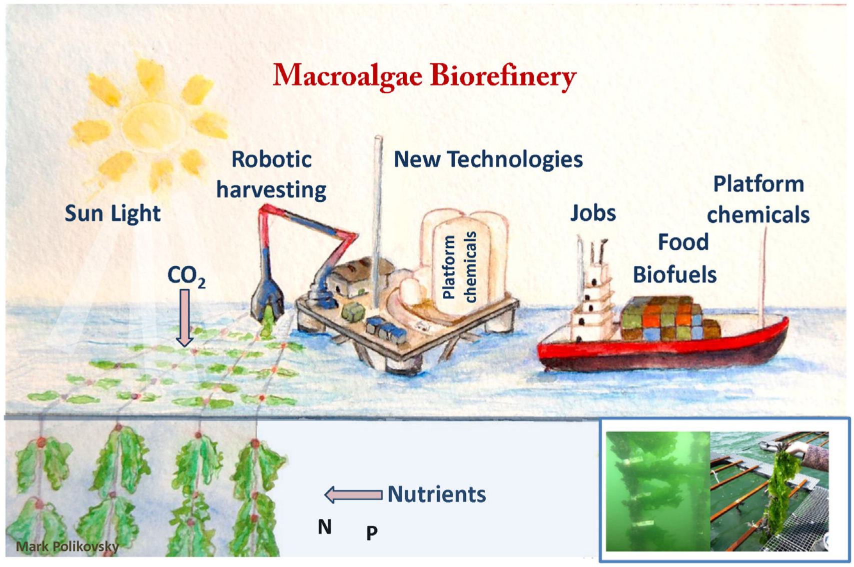

Fig. 1. The concept of off-shore biorefineries for the production of food, platform chemicals, and biofuels. We assume that the cultivation is done by extensive methods with ropes/cages [81]. The opportunity to increase the cultivation depth by mixing was discussed in [8]. Insert on the right shows the example off-shore cultivation of macroalga from *Ulva* genus [9].

biofuels show higher potential yield in Life Cycle Assessment and are easier to harvest [21]. The higher carbohydrate content of macroalgae also make them suitable for bioconversion into fuel molecules such as methane [22], hydrogen [23], syngas [24], ethanol [14], n-butanol [25], and 2,3-butanadiol [26]. Still, macroalgal biomass is considered an "untapped" resource which requires further intensive research and development [27–29]. In contrast to terrestrial plants and microalgae, the global potential for macroalgae feedstock for biorefineries has never been estimated.

In this work, we analyze the global potential for offshore macroalgae biorefineries to supply biomass, food, platform chemicals and fuels. As a model system, we took green filamentous macroalgae species from the *Ulva* genus, which can form free-floating mats during blooms [30]. *Ulva* is of particular interest due to fast growth rates, low content of lignin and high content of protein with essential amino acids. To estimate the biomass production potential, we constructed a mathematical model of macroalgae metabolism and growth rate. The model incorporates the main parameters that determine biomass productivity, namely illumination, water temperature, salinity, nitrogen, and phosphorous. These parameters are derived from climatological satellite and in-situ data. We estimated the possible production of total biomass, ethanol, butanol, acetone, methane and proteins at newly defined global provinces. In addition, based on the energy requirements for transportation and biomass moisture content, we developed the model that predicts the distance of the offshore biomass cultivation facility from the processing facility. Finally, we discuss the risks and sustainability aspects of large-scale, offshore biomass production.

2. Methods

2.1. Metabolic model of Ulva growth

We estimated the biomass production potential using a mathematical model of metabolism of *Ulva*, modified from [31–33]. We assumed that the macroalgae cultivation is extensive using traditional ropes/cages methods. In the previous work, we discussed the possibility to significantly increase the *Ulva* biomass yield using mixing systems for the free floating thalli, which allow for increasing the cultivation depth [8]. Model parameters are shown in Table S1. We run the model on a global 1°grid with one output file for each month of the year. Algae growth rate (μ) is calculated as a function of light intensity (I), temperature (T), salinity (S) nutrients (N and P for nitrate and phosphate, respectively) and respiration rate (r_{resp}):

$$\mu = \mu_{max} \cdot f(I, T, S, N, P) - r_{resp}. \tag{1}$$

In this model we assume that each of the factors has a separate impact on the biomass growth rate. Therefore, the approximated function for biomass growth rate appears in Eq. (2):

$$\mu = \mu_{max} \cdot f(I) \cdot f(T) \cdot f(S) \cdot f(N) \cdot f(P) - r_{resp} \tag{2}$$

where μ_{max} (which is a function of the stocking density [34]) (d^{-1}) is maximum growth rate, r_{resp} the respiration rate (d^{-1}) defined as

$$r_{resp=}r_{resp20}\theta^{T-20} \tag{3}$$

where r_{resp20} is the maximum respiration rate at 20 °C, and θ is the empirical factor.

and $f(I, T, S, N, P)$ is defined as follows in Eqs. (4)–(8) under the assumption the concentration of nutrients (N and P) is maintained constant, which can be achieved, for example, by artificial upwelling systems [82,83]:

$$f(I) = \frac{I}{I_{opt}} e^{\left(1-\frac{I}{I_{opt}}\right)} \tag{4}$$

where I is the illumination at time (t) and I_{opt} is the optimum illumination for *Ulva* biomass accumulation.

$$f(T) = e^{-2.3\left(\frac{T-T_{opt}}{T_x-T_{opt}}\right)^2} \tag{5}$$

where

$T_x = T_{min}$ *for* $T <= T_{opt}$ and $T_x = T_{max}$*for* $T > T_{opt}$

For $S > 5$

$$f(S) = 1-\left(\frac{S-S_{opt}}{S_x-S_{opt}}\right)^m \tag{5}$$

where

$S_x = S_{min}$ and $m = 2.5$ for $S < S_{opt}$
$S_x = S_{max}$ and $m = 2$ for $S >= S_{opt}$.

For $S < 5$

$$f(S) = \frac{S - S_{min}}{S_{opt} - S_{min}}. \tag{6}$$

For ($N > N_{min}$) and ($P > P_{min}$):
For N:
If 12 < N:P and N:P < 20:

$$f(N,P,C) = 1.$$

If N:P < 12 f(N,P,C) = f(N):

$$f(N) = \frac{N_{int} - N_{int\_min}}{keq + N_{int} - N_{int\_min}}$$

If N:P > 20 f(N,P,C) = f(P):
If $P_{int} < P_{int\_max}$:

$$f(P) = \frac{P_{int}}{P_{int\_max}}.$$

If $P_{int} > P_{int\_max}$:

$$f(P) = 1.$$

Daily production per m^2 of FW biomass is derived by multiplying calculated growth rate (μ) with biomass density (σ), kg m^{-2}) [34], Eq. (7):

$$BM_{FW} = \mu \cdot \sigma. \tag{7}$$

2.2. Global mapping of environmental conditions enabling biomass growth

Global monthly values of sea surface salinity, temperature, and nutrients (phosphate and nitrate) are extracted from the World Ocean Atlas (WOA) 2013 [35–37]. The dataset consists of objectively analyzed climatologies of in-situ measurements projected on a 1° grid. WOA data is downloaded from the national center for environmental information (https://www.nodc.noaa.gov/OC5/woa13/).

For solar illumination we use global monthly climatologies of photosynthetically active radiation (PAR) from the Moderate Resolution Imaging Spectroradiometer (MODIS) aboard the Aqua satellite. The data are obtained from the ocean color data distribution site (http://oceandata.sci.gsfc.nasa.gov/). PAR values are daily-averaged estimates of downwelling flux of photons just below the sea surface, integrated over the wavelength range of 400-to-700 nm. The data, which has a spatial resolution of 9 km, is gridded on the 1° grid of the WOA dataset.

2.3. Characterization of offshore biorefinery provinces

We define offshore biorefinery provinces as areas extending up to 400 km from the shore and, according to our model results, have the potential for production of biomass. Overall, we identify 13 such provinces, which are partitioned into two groups: deep water provinces — those in which biomass production is only possible at water depth of more than 100 m (for systems mooring), and shallow water provinces, in which biomass production is possible at water depth of 100 m or less (blue and red boxes in Fig. 3, respectively). We define the latter, which meet the important 100 m depth criteria for near future offshore aquaculture systems mooring [38], as near-future deployable biorefinery provinces (NDBP). The near future term here is used in the context of a reserve base: possible but marginally economic resource, which can be used in the next 50 years. The 13 offshore biorefinery provinces and their abbreviations (in brackets) are detailed in Table 1.

2.4. Ulva biomass based biorefinery for the production of food protein, platform chemicals, and energy carriers

Macroalgae can be converted into multiple products via chemical and biochemical pathways. The production methods for each product are specific and are optimized according to market demand. In this work we estimated the production potential of ethanol, butanol, acetone, methane, and proteins from *Ulva* biomass. The production of ethanol, butanol, acetone, and methane is achieved by fermentation, and proteins can be produced by extraction. The yields of derived products are calculated by multiplying dry weight biomass with the conversion factors, ranges of which depend strongly on the environmental parameters during biomass growth, are detailed in Table S2. Dry weight (DW) of the *Ulva* biomass is calculated as wet weight (Eq. (7)) divided by 6.

$$BM_{DW} = BM_{FW}/6. \tag{8}$$

3. Results and discussion

3.1. Exergy efficiency of a single marine biorefinery

Offshore marine biorefineries have the potential to complement the terrestrial agriculture in the production of raw materials for various industries. However, the fundamental property of these refineries to become reality is their exergy efficiency. In a previous work, we introduced the theoretical background of exergy efficiency of bioenergy systems and demonstrated this approach analyzing European agricultural bioenergy sector [39]. Exergy efficiency, which is decreasing the destroyed physical, economic, and environmental exergy, will predicate the economic and environmental feasibility of biorefinery systems in the coming years [39]. However, unlike terrestrial bioenergy systems where a lot of data is available, lack of information prevents the detailed analysis of exergonomics for offshore biorefineries today [39]. The following theoretical estimations can be used to determine the basic design constraints on the offshore biorefineries. The net energy balance for the marine biorefineries is shown in Eq. (9):

$$\sum_{p=1}^{n} E_p = AQ_s - E_{ph} - E_c - E_t - E_{cov} - E_{dis} \tag{9}$$

where E_p (MJ) is the energy density of all products produced by marine biorefinery, A (m^2) is the total cultivation area, Qs (MJ/m^2) is the local solar irradiance, E_{ph} (MJ) is the energy lost on photosynthesis, E_c (MJ) is the energy invested for biomass cultivation, E_t (MJ) is the energy invested in transportation, E_{con} (MJ) is the energy invested in

Table 1
Offshore biorefinery provinces and their abbreviations.

Near-future deployable biorefinery provinces (NDBP)	Deep water biorefinery provinces
East Asia offshore waters (EAS)	Central America offshore waters (CAM)
North Atlantic (NAT)	Indian Ocean (IND)
South America offshore waters — East (SAE)	Kerguelen (KRG)
South America offshore waters — West (SAW)	New Zealand (NEZ)
West Africa offshore waters — South (WAS)	North America offshore waters — West (NAW)
	North America offshore waters — South (NAS)
	Tasmania (TAS)
	West Africa offshore waters — North (WAN)

conversion of the biomass into products, and E_{dis} (MJ) is the energy invested in distribution. The goal of the engineering efforts today in all fields of bioenergy and biorefineries is to decreases the sum of E_{ph}, E_c, E_t, E_{cov} and E_{dis} (MJ) to maximize the useful energy produced by the biorefinery. Previously, we derived the equations for the optimum size, capacity, and efficiency of a single biorefinery [40]:

$$\eta_{\max} = 1 - \frac{E_{\min}}{Q_s (nD_{opt})^2} \tag{10}$$

where E_{min} is the minimum wasted energy ($E_{ph} + E_c + E_t + E_{con} + E_{dis}$), n is the specific area in the characteristic space with dimension D occupied by biomass farming and D_{opt} is calculated as in [40]. Our results show that under given photosynthetic efficiency (E_{ph}), extensive natural growth (no energy is invested in cultivation E_c), and current state of the art of biomass conversion efficiency to products (E_{con}), the size and efficiency (and thus economic feasibility) of a single biorefinery are constrained by the size (D) of a territory this biorefinery brings the raw material from and distance the products are delivered to its users ($E_t + E_{dis}$). The numerical detailed analysis of large-scale open ocean offshore marine biorefineries today is not possible as these systems do not exist. However, in the following sections we will discuss the potential of the offshore marine biorefineries and show their practical constrains due to the energy required for biomass transportation.

3.2. Global and regional potential for offshore biomass production

Global projection of the model results shows that theoretically, without taking into consideration any technological or ecological limitations, *Ulva* biomass can be produced in approximately 10% of the World Ocean (Fig. 2A), largely in regions that are relatively rich in nitrate and phosphate as the north Pacific and north Atlantic subpolar gyres, southern Ocean and eastern equatorial Pacific [41].

The potential of the offshore biorefinery to produce biomass and various products critically depends on the cultivation stocking density with variation of the yields in the order of magnitude (Table 2). Previous experimental studies in Denmark in the on-shore systems, showed that the optimum stocking density for *Ulva* cultivation is 4 kg m^{-2} [42]. In the detailed follow-up calculation examples, we chose to work with this stocking density for cultivation. However, the practical density will depend on the location, species of choice, and potential environmental impacts, as discussed in the following paragraphs. At 4 kg m^{-2} stocking density, the global annual biomass production potential is ~10^{11} ton DW y^{-1}, and the total theoretical primary energy of *Ulva* biomass from the offshore cultivation is 2052 EJ $year^{-1}$ (Fig. 2A and Tables 2, 3, based on the low heating value) LHV(for *Ulva* of 19 MJ per kg DW [43]). The total theoretical primary energy of *Ulva* biomass from the shallow, near-shore waters cultivation is 18 EJ $year^{-1}$ (Table 3). In comparison, the global potential of energy crops for biofuels is estimated at 125–760 EJ per year [44].

The deployment of biomass cultivation systems in the ocean is a highly complex problem whose feasibility depends on technological readiness and on environmental factors, like water depth and distance from the shore [38]. Limiting the area used for oceanic biomass cultivation according to these two environmental parameters may lead to more than 4 orders of magnitude differences in the global production potential (Fig. 2B). Additional important factor such as wind, wave and currents will pose additional constrains on the specific location productivity. We found that with the technologies available for offshore cultivation in the near-future, which require water depth of less than 100 m for mooring [38] (red spot in Fig. 2B), there is almost no impact on the farms distance from shore. Importantly, at this depth range practically all the biomass can be cultivated in farms located less than 400 km from the shore, and are thus bounded within the Exclusive Economic Zones (EEZ) [38].The global potential of the near-future achievable deployment offshore biomass production (i.e. in regions extending up to 400 km distance from the shore, and with water depth of up to 100 m) can provide $9.4 \cdot 10^8$ ton DW y^{-1}. This is equivalent to 17.9 EJ y^{-1} of primary energy potential (calculated as LHV). In comparison, the predicted bioenergy potential from agricultural land in 2050 is expected to be 64–161 EJ y^{-1} [45]. It is important to point out that the numbers reported here are based on the total potential assessment of ocean areas, and there is no technology available today to utilize these areas.

Almost all of the biomass production potential at a distance smaller than 400 km from shore is concentrated at 13 provinces (Fig. 3A). Approximately 85% of the production potential at this distance from the shore is associated with 5 regions that are characterized by water depth of up to 100 m (red boxes in Fig. 3A). These regions, which meet the important water depth criteria for mooring offshore cultivation platforms using near future technologies, are hereafter defined as near-future deployable biorefinery provinces (NDBP, see details in Section 2). For each NDBP we extract monthly values of productive surface area (S, Fig. 3B), defined as the extension of the region allowing biomass production and meeting the 100 m water depth and 400 km distance from shore criteria, and spatially averaged biomass productivity (DW_{mean}, Fig. 3C). Total biomass productivity (DW_{tot}, Fig. 3D), is calculated by multiplying S with DW_{mean}. As for the global patterns of biomass production potential (Fig. 2a), NDBPs are associated with regions of elevated nutrient concentrations at the ocean's surface layer

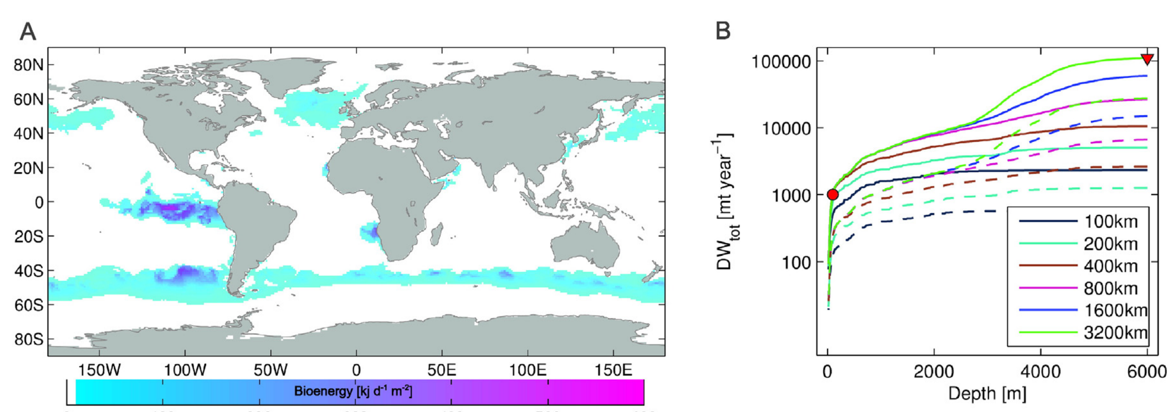

Fig. 2. Global potential for offshore biorefinery. A) Potential for daily production of bioenergy over the World Ocean, taking an optimum biomass stocking density of 4 kg m^{-2}. Values in the map will change with changes in stocking density (Table 2) in nonlinear way [43]. B) Impact of water depth and distance from the shore on total biomass production potential, taking biomass stocking density of 1 kg m^{-2} and 4 kg m^{-2} (dashed and solid lines, respectively). Red circle marks the 100 m depth and 400 km distance that define the limits for near-future offshore cultivation. Red triangle marks global potential regardless of any depth or distance from coast limitation.

Table 2
Potential for offshore production of biomass and derived products for various cultivation stocking densities. The notion “All waters” refers to all locations regardless of water depth and distance from the coast, while “Shallow near shore waters” refers to areas associated with water depths smaller than 100 m and located less than 400 km from the coast. Conversion factors are detailed in the Supplementary information Table S1. The experimentally found optimum stocking density [34] is highlighted in the table. The ratio of biomass yields at various stocking densities cultivation is based on the experimental data in [43].

Biomass stocking density	1 kg m^{-2}		2 kg m^{-2}		4 kg m^{-2}		6 kg m^{-2}		8 kg m^{-2}	
	All waters	Shallow near shore waters	All waters	Shallow near shore waters	All-waters	Shallow near shore waters	All-waters	Shallow near shore waters	All-waters	Shallow near shore waters
Biomass [10^6 t $year^{-1}$] (DW)	67,500	591	81,000	710	108,000	946	54,000	473	40,500	355
Ethanol [10^6 t $year^{-1}$]	2025–15,525	18–136	2430–18,630	21–163	3240–24,840	28–218	1620–12,420	14–109	1215–9315	11–82
Butanol [10^6 t $year^{-1}$]	2025–4050	18–35	2430–4860	21–43	3240–6480	28–57	1620–3240	14–28	1215–2430	11–21
Acetone [10^6 t $year^{-1}$]	675–1350	6–12	810–1620	7–14	1080–2160	9–19	540–1080	5–9	405–810	4–7
Methane [10^6 m^3 $year^{-1}$]	675–6480	6–57	810–7776	7–68	1080–10,368	9–91	540–5184	5–45	405–3888	4–34
Protein [10^6 t $year^{-1}$]	3375–16,200	30–142	4050–19,440	35–170	5400–25,920	47–227	2700–12,960	24–114	2025–9720	18–85
Energy [10^{12} kJ $year^{-1}$]	1,282,500	11,234	1,539,000	13,481	2,052,000	17,974	1,026,000	8987	769,500	6740

(Fig. 3a). These elevated nutrient levels result from a variety of dynamical processes as coastal upwelling (e.g. provinces SAW and WAS) and deep wintertime convection (e.g. province NAT), which upwell nutrient rich waters from below the mixed layer [46]. Monthly variations in surface area and potential biomass productivity, which are characteristic to all NDBPs, are driven primarily by seasonal variations in Photosynthetically Active Radiation (PAR) and in nutrient availability. The potential for biomass production in the different NDBP is limited for periods of between 8 (provinces SAE and SAW) and 10 (province WAS) months.

3.3. Offshore production of macroalgae-derived proteins

Deployment of large-scale offshore biorefineries opens the way to produce ingredients for soaring food and animal feed markets. The global demand for plant proteins is expected to grow from $4.73 \cdot 10^8$ in 2014 to $9.44 \cdot 10^8$ ton protein in 2054 [47]. This growth in protein demand is expected to require additional $100 \cdot 10^6$ arable land hectares [47]. Based on the previous studies that determined the nutritional value of *Ulva*, and which included its protein content [48–50], our model predicts that the global potential of marine biomass to produce protein is $5.4 \cdot 10^9$ –$25 \cdot 10^9$ ton per year (Table 3). The near-future deployable offshore marine biorefineries could produce in total $0.47 \cdot 10^8$ –$2.27 \cdot 10^8$ ton protein per year. Thus, offshore produced proteins have the potential to reduce by 5–24% terrestrial proteins production and, consequently, the requirements for agricultural land required for proteins production. Previous experiments of *Ulva* proteins for the animal feed have already shown that *Ulva* can be used for aquaculture [51], lamb, [52] and broiler chicken [50] feed. Furthermore, *Ulva* protein contains essential-to-humans amino acids, which are not available in the most widely used soy proteins as lysine, valine, threonine, and tryptophan [48]. However, protein extraction technologies, optimized for the soy proteins during last five decades, still must be developed for macroalgae.

3.4. Offshore production of macroalgae-derived platform chemicals

In recent years economic, political, and sustainability factors drive the development of alternative pathways to produce platform chemicals and fuels from local, non-fossil sources. Biomass conversion is a near-medium solution for an inevitable shift towards low-carbon economies. Here we analyze the potential of biorefineries based on off-shore cultivated *Ulva* to provide for the key platform chemicals ethanol, butanol and acetone, which can be used as fundamental building blocks for the chemical and energy industries. Ethanol is an important player in the chemical industry as precursor to such organic molecules as ethyl halides, diethyl ether, and acetic acid. It is also already an important component of the transportation biofuels market. Furthermore, it can be converted by catalytic conversion to light olefins to longer chain alkenes/alkanes, which can replace currently used petroleum [53]. Sustainable pathways for the ethanol production from biomass are the key challenge for this industry [54]. Global ethanol production in 2014 peaked at $9.1 \cdot 10^7$ ton. Assuming the yields from the currently available conversion methods, the near future and total potential for marine biorefinery based on *Ulva* to produce sustainable bioethanol is $2.8 \cdot 10^7$ –$2.2 \cdot 10^8$ and $3.2 \cdot 10^9$ –$2.5 \cdot 10^{10}$ ton per year, respectively (Table 3). In comparison, the global potential for the bioethanol production from wasted crops is estimated at $3.8 \cdot 10^7$ ton ethanol per year [55].

Table 3
Potential for offshore production of biomass and derived products for the near-future deployable biorefinery provinces (NDBP) at the optimum biomass density of 4 kg m^{-2} [34]. Conversion factors are detailed in the Supplementary Information Table S1. The notion “All waters” refers to all locations regardless of water depth and distance from the coast, while “Shallow near shore waters” refers to areas associated with water depths smaller than 100 m and located less than 400 km from the coast.

	All waters	Shallow near shore waters	EAS[a]	NAT[b]	SAE[c]	SAW[d]	WAS[e]
Biomass [10^6 t $year^{-1}$] (DW)	108,000	946	435	124	110	62	82
Ethanol [10^6 t $year^{-1}$]	3240–24,840	28–218	13–100	4–29	3–25	2–14	2–19
Butanol [10^6 t $year^{-1}$]	3240–6480	28–57	13–26	4–7	3–7	2–4	2–5
Acetone [10^6 t $year^{-1}$]	1080–2160	9–19	4–9	1.24–2.48	1.10–2.20	0.62–1.23	0.82–1.64
Methane [10^6 m^3 $year^{-1}$]	1080–10,368	9–91	4350–41,760	1240–11,904	1100–10,560	615–5904	820–7872
Protein [10^6 t $year^{-1}$]	5400–25,920	47–227	22–104	6–30	6–26	3–15	4–20
Energy [10^{12} kJ $year^{-1}$]	2,052,000	17,974	8265	2356	2090	1169	1558

[a] EAS — East Asia offshore waters.
[b] NAT — North Atlantic.
[c] SAE — South America offshore waters — East.
[d] SAW — South America offshore waters — West.
[e] WAS — West Africa offshore waters — South.

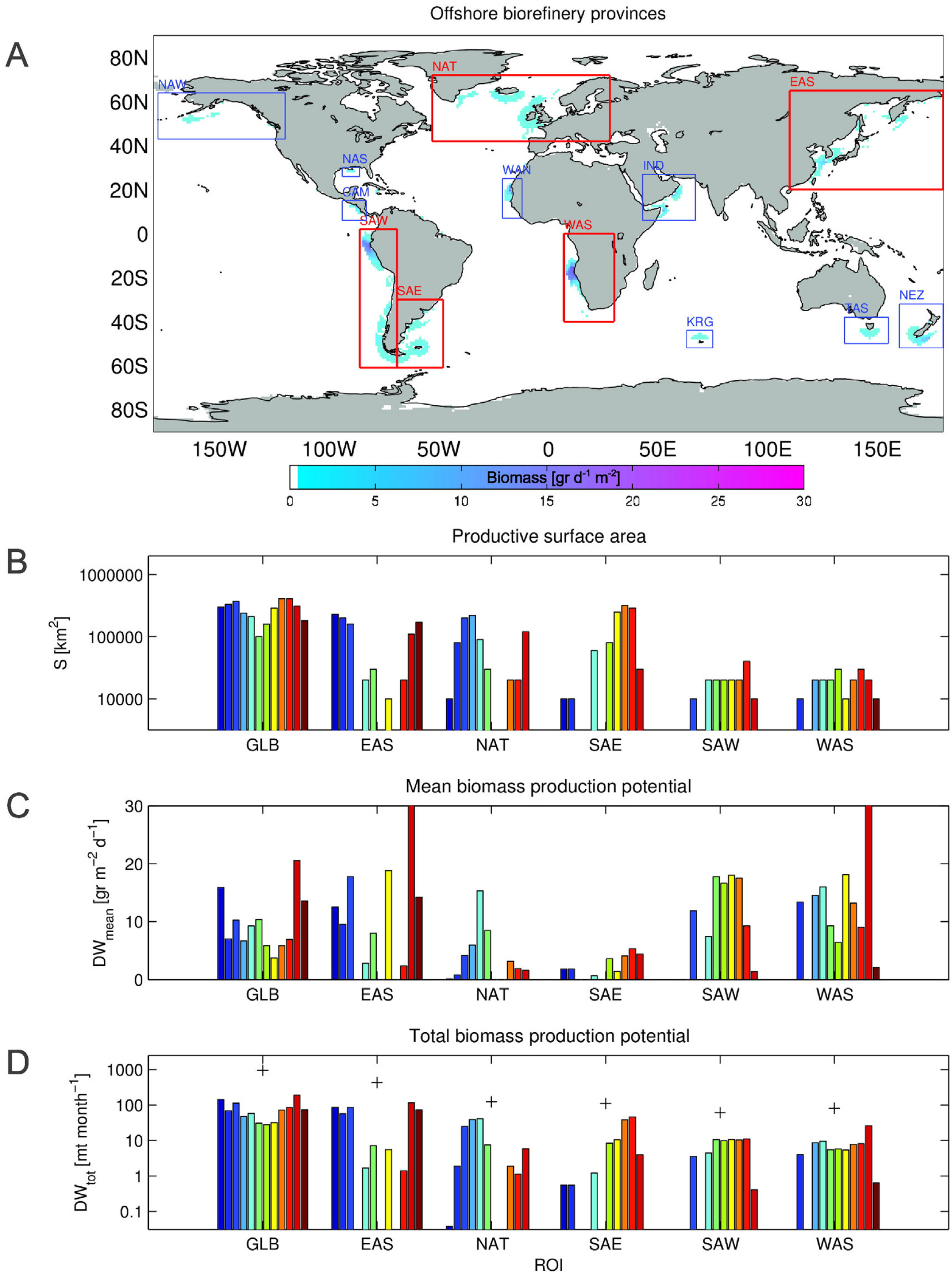

Fig. 3. Regional potential for offshore biorefinery. A) Potential for biomass production at a distance of less than 400 km from land, taking biomass stocking density of 4 kg m^{-2}. Values in the map will change with changes in stocking density (Table 2). Boxes delineate major offshore biorefinery provinces, with those permitting biomass production at water depth of up to 100 m (defined as near-future deployable biorefinery provinces — NDBP) marked in red, and those permitting biomass production only at deeper waters marked in blue. (B–D) Monthly estimates of (B) productive surface area; (C) mean biomass production potential; and (D) total production potential within the 5 NDBP (red boxes and associated abbreviations in panel A) and integrated globally (denoted GLB). Colors denote different months of the year. The analysis is performed over locations associated with water depth of 100 m or shallower. The + signs mark annually integrated biomass production potential at each region. Assumed biomass density of 4 kg m^{-2}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The expected demand for butanol in 2018 is $4.9 \cdot 10^6$ ton per year [56], and the predicted 2020 demand for acetone is $7.2 \cdot 10^6$ ton acetone per year [57]. Assuming the yields from the already demonstrated ABE (acetone–butanol–ethanol) *Ulva* fermentation, global offshore *Ulva* based biorefineries could provide $3.2 \cdot 10^9$ –$6.5 \cdot 10^9$ ton butanol and $1.1 \cdot 10^9$ –$2.1 \cdot 10^9$ ton acetone per year. The near-future cultivation and processing technologies could generate $2.8 \cdot 10^7$ –$5.7 \cdot 10^7$ ton butanol per year and $9 \cdot 10^6$ –$1.8 \cdot 10^7$ tons of acetone per year (Table 3). These estimations show that marine biomass feedstock has the real potential to provide an alternative to terrestrial crops for the production of platform chemicals, thus reducing the burden on the arable land and increase the land surface available for food crops production.

3.5. Offshore production of macroalgae-derived biofuels

We also analyzed the potential of *Ulva* based biorefineries [40,58] to provide energy for the transportations sector. In 2010 the global transport sector consumed almost $2.2 \cdot 10^6$ ton of oil equivalent (toe), with about 96% of this coming from oil [59]. Because of population growth and life style changes, World Energy Council predicts an increase of 30–80% in the total fuel demand by 2050, resulting in expected demand of $2.86–3.94 \cdot 10^6$ toe [59]. The total energy consumption of the transportation sector is predicted to consume 125–170 EJ y^{-1}, of which 52–80% will be derived from oil based gasoline and diesel [59]. Because of the intrinsic limitations discussed above, terrestrial based biofuels could provide 12–24% of the future transportation needs. Using currently available ethanol fermentation processes, the near-future and total global potential of offshore biorefineries for production of transportation biofuels, is estimated at $1.8 \cdot 10^7 – 1.3 \cdot 10^8$ toe and $1.5 \cdot 10^9 – 2.1 \cdot 10^9$ toe respectively (under the assumption that 1 ton of bioethanol = 0.64 toe). These results are encouraging, as they show for the first time that even using currently available technologies, the biorefineries could displace fossil fuels in the transportation sector, thus stabilizing the greenhouse gases emissions.

In addition, the near-future and global potential of *Ulva* based biorefineries could generate $9.4 \cdot 10^9 – 9.1 \cdot 10^{10}$ m^3 and $1 \cdot 10^{12} – 1 \cdot 10^{13}$ m^3 methane per year, respectively. This is equal to $9.4 \cdot 10^{10} – 9.1 \cdot 10^{11}$ kWh and $1 \cdot 10^{13} – 1 \cdot 10^{14}$ kWh, assuming 10 kWh per 1 m^3 of gas. This biogas has a potential to displace $5.1 \cdot 10^7 – 4.9 \cdot 10^8$ and $5.8 \cdot 10^9 – 5.6 \cdot 10^{10}$ ton of new CO_2 emissions from the natural gas, assuming 0.54 kg of CO_2 per kWh.

3.6. The size limitation and the limitation of an offshore cultivation site location from the shore and processing facility

Previous studies on the cost function agricultural processing systems [60] and our biorefinery energy efficiency analysis based on the served territory size [40] show that feedstock transportation costs limit the size of the biorefinery. Transportation costs limit the maximum possible distance of the cultivation site to the processing facility. However, different from the near-shore facilities, where the costs on biomass transportation from the sea to the on-shore processing facility are known (~30% of the macroalgae costs [61]), the real monetary transportation costs from the open ocean off-shore biorefineries can be only estimated. A more realistic approach is to estimate the energy expenses required for transportation that will limit the distance of an offshore cultivation site from the processing facility.

The maximum economic distance from the processing facility of an offshore cultivation area is calculated using Eq. (11):

$$D_t = \frac{\varepsilon \sum_{p=1}^{n} E_p}{2E_t} \tag{11}$$

where D_t (km) is the maximum economic transportation distance, and ε is the ratio of the energy embedded in the final products that can be used for transportation of the feedstock to keep the process economically viable. Here we assume that the transportation vessel make only one direction with cargo and is empty on its way back.

To exemplify the estimation the transportation energy constrains of the off-shore cultivation, following [62], we assumed that the transportation will be done with Aframaxship tanker. The tanker capacity is 100,000 tons and the average fuel consumption (between full and empty cargo) is 25.4 gal km^{-1} (4019.55 MJ km^{-1}) of heavy ship oil (based on MT Tempera data http://www.laivakuvat.com/en/mt-tempera/). Previous extensive studies in the bioethanol industry showed that for profitability and positive net energy balance, the energetic cost of transportation should be at ~1.8% of the total energy embedded in the final products, distributed equality between biomass transportation and final products distribution [63]. Therefore, we constrained the total energy expenditures (ε) on transportation on 0.9% of the energy embedded in the potential products of the transported macroalgae biomass. In addition, we assumed that only energy produced from ethanol, butanol, and acetone could be used for transportation. Table S3 summarizes the parameters used for transportation energy expenditures simulation. The simulation results that connect the transported macroalgae DW content with the distance of the offshore cultivation facility from the biorefinery appear in Table 4. In the situation when the biomass is not processed directly near the cultivation site or on the vessel, our results show that dehydration of the biomass on the cultivation site on the ship is required to increase the distance of the offshore cultivation site from the processing facility without compromising the energy efficiency of the process (Fig. 4).

The ratio between the DW ratio of the transported macroalgae biomass is expressed in Eq. (12):

$$D_t = 689.6 m_{DW} \tag{12}$$

where m_{dw} is the DW content of the transported biomass.

The estimated Dt also poses the limits to the size of the future offshore farms. Assuming the offshore processing facility, as shown in Fig. 1, and homogeneous cultivation circular area around the central processing platform and transportation done by Aframaxship tanker, the farm area (A, km^2) can be calculated with Eq. (13).

$$A = \pi D_t^2. \tag{13}$$

Therefore the maximum economic area of the farms, constrained by the transportation energy consumption, for fresh macroalgae biomass harvesting will be $\sim 41 \cdot 10^3$ km^2.

To the best of our knowledge, the portable technology for onsite biomass dehydration is not yet available and should be the focus of the further studies for all types of biorefineries. Further improvement of the biomass conversion, which today requires most of the energy in the biomass value chain (52% of produced energy is required for conversion processes in the case of corn bioethanol) [63], will further increase the distance between the cultivation and processing site. Nevertheless, it is important to point out that biomass dehydration is by itself an energy intensive process that could change the total energy return on investment of the biorefinery. Recent development of new dehydration technologies, such as pulsed electric fields, was shown to reduce energy consumption required for biomass dehydration by 30–50% [64].

3.7. Sustainability of offshore biorefineries

The sustainable implementation of marine biorefineries at the large scale requires to address fundamental environmental and social implications. Important factors that should be taken into consideration are

Table 4
Maximum economic biomass transportation distance with Aframaxship tanker. Assuming conversion factors as appear in Table 4.

Cargo DW [ton]	Harvested macroalgae wet weight [ton]	Ethanol [ton]	Butanol [ton]	Acetone [ton]	D_t [km]
100,000	600,000	14,000	6000	2000	690
50,000	300,000	7000	3000	1000	345
33,333	200,000	4667	2000	667	230
25,000	150,000	3500	1500	500	172
20,000	120,000	2800	1200	400	138
16,667	100,000	2333	1000	333	115

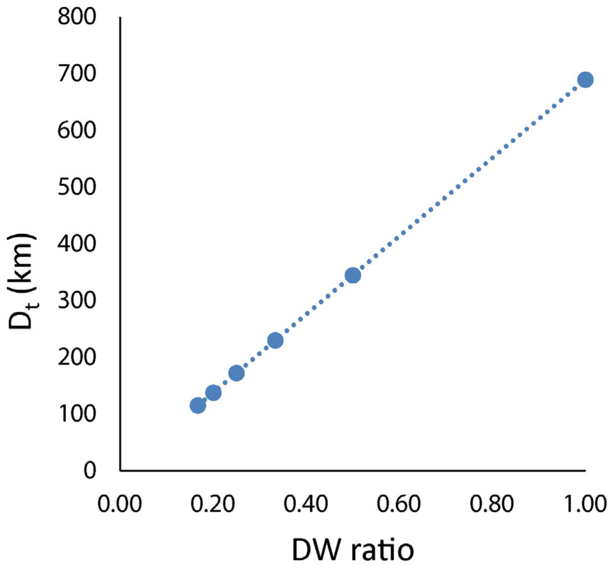

Fig. 4. The dependence of maximum economic distance of an offshore cultivation area from the processing facility with transportation done by Aframaxship tanker with 100,000 tons capacity.

marine protected zones, where deployment of macroalgal cultivation systems is not possible. Moreover, the very large scale offshore systems may have strong ecological consequences, as affecting species migration patterns and ecosystem community structure. Concerning the possible social impacts, marine biorefineries could transform the economies of the low income farmers, as the major macroalgae cultivation today is done on the family level, by poorest farmers, mostly in Indonesia, Philippines, China, India and Tanzania, who earn from $0.5 to $3 a day [61]. The macroalgae are cultivated in the near shore facilities and are sold fresh, dried and semidried for processing, mostly for food ingredients industry. The cost of macroalgae biomass at the farm today varies from $500 to $700 DW ton, while the final extracted products are sold for an order of magnitude more [61]. Moreover, only 8–12% of the cultivated biomass is used for the food chemicals production, the rest is disposed as waste. Development of new technologies for cultivation in the near-future explorable areas, and macroalgae processing to platform chemicals, food and fuels have a potential to transform this industry leading to the creation of new, high professional jobs, and, thus, providing for additional income and technological profession to the thousands of families who are already involved in macroalgae farming [61].

The major challenges with the exploration of the offshore areas for cultivation are technology, economics and policy. The current concepts of offshore marine biomass cultivation include Near Farm Concepts for kelp growth [65], Tidal Flat Farms, Floating Cultivation [65], Ring Cultivation [66] and most recently wind-farm integrated systems [67]. Additional cultivation methods are required to enable the deployment of offshore oceanic areas. Although significant advancements have been achieved in recent years with synthetic biology tools, the complete conversion of marine macroalgae derived biomass into chemicals is still challenging [6,7,68]. In addition, our model shows that the potential of the offshore biorefineries to produce biomass in neutral waters may be two orders of magnitude larger than that of waters bounded within EEZ, thus imposing a large regulation challenge for the allocation and taxation of these productive areas. Therefore, further deployment of offshore biorefineries requires both technological and regulation development to allow for exploration of ocean areas in the neutral waters.

Several previous works made an attempt to estimate the costs of the cultivation in the open ocean offshore facilities, reviewed in [9]. The estimated costs of infrastructure (using ropes cultivation method) in Europe is between 57,000 and 170,000 $/ha [9]. The estimated cost of production of 1 ton (DW) of macroalgae in Europe is in the 1134–1700$/ton (DW) range [9]. Novel economic model, should be developed to assess the costs of bringing open-ocean-cultivated macroalgae to the market place at a scale and cost-competitiveness to meet global transportation fuel, by-product, and food demands.

3.8. Environmental risk from offshore macroalgae cultivation

Large scale cultivation can be responsible for positive and negative impact on coastal and marine ecosystems [11]. Therefore, the balance is necessary to attained in between biomass for chemicals, food and fuels production and its environmental cost [27]. Compared to other terrestrial biomass crops, macroalgae have higher rate of carbon dioxide fixation, which is a potential benefit of large scale cultivation [69]. At the same time, there are many environmental risks associated with large scale offshore macroalgae cultivation. Fig. 5, shows the entire framework of risk management for offshore macroalgae cultivation. This framework is divided in three sections. Section 1 shows the risk prevention or the possible risks which can be prevented before the cultivation or during the cultivation period. Section 2 shows the risks that can be controlled during biomass harvesting and conversion. Section 3, shows the risks which require mitigation as they could potentially impact the surrounding ecosystems during the large scale cultivation of the biomass.

Many environmental factors such as winds, waves, ocean currents, and rain may impact adversely the cultivation, but their effect can be somewhat controlled by selecting favorable sites for cultivation (Fig. 5). Natural disasters such as storms, hurricanes, typhoons, tsunami, are generally unpredictable and can destroy cultivation totally. Types of seabed under the water, the depth of sand, possible grazers are predictable and can be analyzed before selecting sites. All these factors are avoidable, thus the risks associated with these factors can be reduced.

Risks from the factors like light, nutrients, salinity level of marine water can be controllable by the selection of macroalgal species tolerable to specific environmental conditions. Successful management of the risks related with these factors is essential for the choice of the site for the implementation of the offshore biorefineries with possibilities of many social and environmental benefits [70].

The large scale cultivation of *Ulva* can strip off all essential nutrients in the immediate vicinity, thus having a negative impact on the entire marine ecosystem. Artificial mixing could balance the reduction in nutrient stocks due to biomass cultivation [71]. In contrast, delay in harvesting, loss of the biomass from the cultivation systems and lack of local grazers could lead to local eutrophication [72].

The dense and large quantity of macroalgae cultivation can restrict circulation in the marine system and reduce gas exchange. In addition, the large scale *Ulva* cultivation could create a shadow inside the marine environment at the cultivation site. This can make light penetration difficult and adversely impact the natural ecosystem of the site. In case of death of macroalgae, the decay of biomass can results in the depletion of oxygen level in the seawater. Leading to the mortality of aquatic life in the marine ecosystem. With this, the decay can release hydrogen sulfide gas [71] with offensive ordure thus polluting the air in the nearby environment. Moreover, macroalgae biomass decay could lead to additional environmental hazards such as formation of toxic concentrations of hydrogen sulphide by sulphate reducing bacteria, which can affect the sensitive marine eco-systems.

The grazing of *Ulva* is dependent on the presence of herbivore grazers at the cultivation site. There are many possible grazers such as bivalves, ascidians, sponges, amphipods, polychaetes, and gastropods. Even the small sized herbivorous fish also acts as grazers which graze on *Ulva* or certain epiphytes on *Ulva*. Grazing can lead to both positive and negative impacts on production and growth of the biomass.

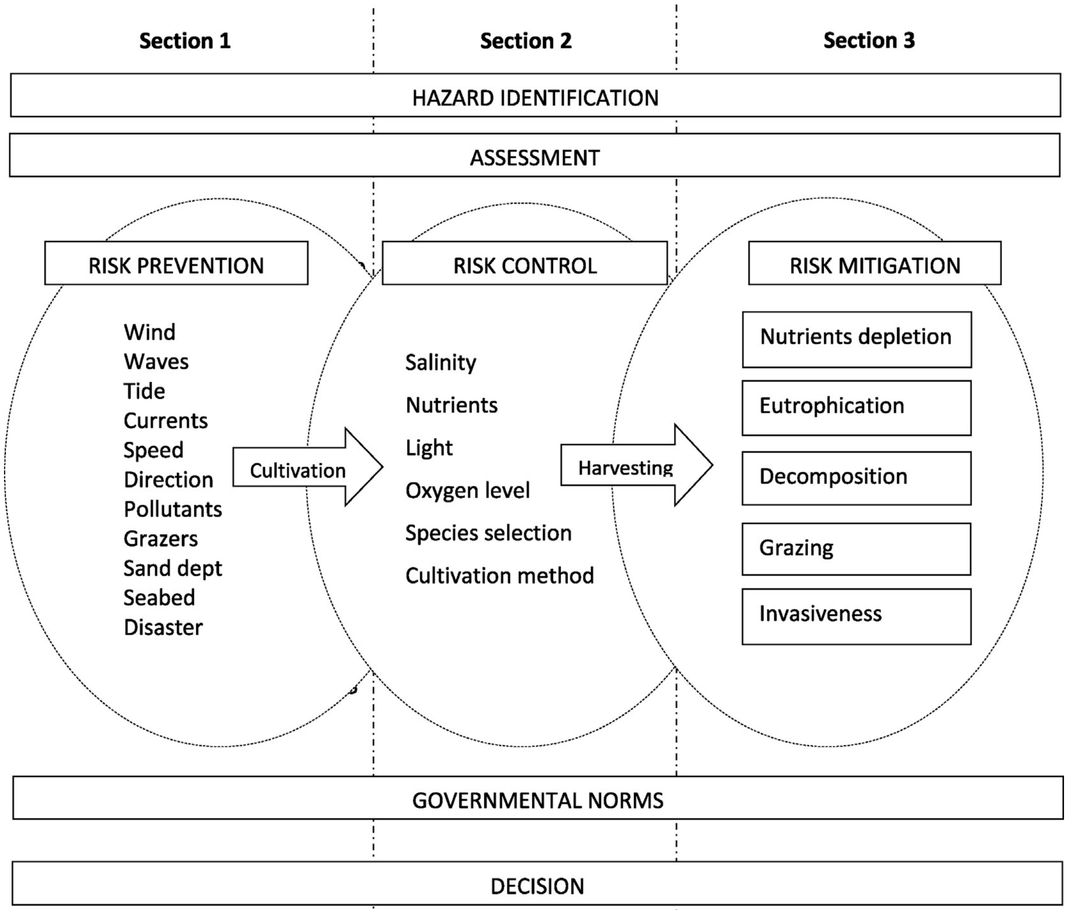

Fig. 5. Entire framework of the risk management for offshore macroalgal cultivation (developed from [80])

Although high grazing results in economical loss, it can mitigate the shading impact of macroalgae growth [73]. The grazing rate depends on the composition of the biomass [74]. It also depends on the other factors such as the presence of dominant grazers, their per capita grazing rate, feeding preferences and patterns of grazing [75]. For example, species of crustaceans can reduce biomass of macroalgae [76] but many invertebrate species generally feed on epiphytes and show positive effect on macroalgal growth. For example, *Gammarus*, which is one of the most important grazer of *Ulva* shows higher grazing on epiphytes present on *Ulva* rather than *Ulva* under high nutrient conditions [77]. Epiphytes are generally grown abundantly at the high nutrient level of seawater and in such case grazers prefer them as food. This thing could counteract the effects of mild eutrophication [78]. Grazers who generally feed on epiphytes, can switch to *Ulva* biomass itself if epiphytes are absent. These complex interactions make it a difficult task to quantify the positive or negative impacts of grazing at monitoring is required at each cultivation site.

An additional environmental risk from large scale macroalgae cultivation, which requires mitigation strategy, is invasiveness, especially if the non-native species are cultivated. For example, in Indian seawater, the non-native macroalgae such as *Gracilaria salicornia* and *Kappaphycus alvarezii* are naturalized and show their occupation and spread [79]. The invasive species can adversely impact on coral reefs, local species of macroalgae and other organisms. There are two approaches available to monitor the invasiveness of macroalgae: 1) low-tech approach, which includes the field surveys and morphological identification of invasiveness; and 2) high-tech approach, which includes DNA analysis, which shows the genetic structure of the population. We have summarized the strategy for risk management of offshore macroalgae cultivation in Table S4.

4. Conclusions

Using a metabolism and growth rate model of the green marine macroalga from *Ulva* genus, coupled with essential inputs from climatological oceanographic data, we analyzed the global potential of offshore biorefineries to provide for biomass, proteins, platform chemicals, transportation fuels and energy. Our results show that even using near-future aquaculture technologies, offshore cultivation of macroalgae has the potential to provide some of the basic products required for human society in the coming decades. This includes displacing entirely the use of fossil fuels in the transportation sector, or providing for 100% of the predicted demand for ethanol, acetone, and butanol, or 5–24% of the demand for proteins or production of biogas that could displace $5.1 \cdot 10^7$ –$5.6 \cdot 10^{10}$ ton of new CO_2 emissions from the power generation from natural gas. In addition to improving offshore cultivation technologies, much attention should be given to study of the ecological consequences of implementing large-scale offshore biorefinery infrastructures, in order to ensure their sustainability and to reduce to minimum their environmental impact. Technological and scientific efforts should be focused primarily on the newly identified near-future deployable biorefinery provinces, NDBP, where offshore biomass cultivation is expected to be most feasible. In summary, based on our model results we conclude that development of sustainable offshore biorefineries infrastructures, if developed carefully, provide a new efficient source for basic products required for human society in the coming decades.

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Appendix A. Supplementary data

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