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Comparative environmental assessment of valorization strategies of the invasive macroalgae *Sargassum muticum*

Paula Pérez-López[1,*], Elena M. Balboa[2], Sara González-García[1], Herminia Domínguez[2], Gumersindo Feijoo[1] and Mª Teresa Moreira[1]

[1] Department of Chemical Engineering, Institute of Technology, University of Santiago de Compostela. 15782 - Santiago de Compostela, Spain

[2] Department of Chemical Engineering, Faculty of Sciences, University of Vigo, As Lagoas s/n, 32004 Ourense, Spain

Abstract

The invasive brown seaweed *Sargassum muticum* (Yendo) exhibits a significant content of phenolic compounds, polysaccharides and fucoxanthin, with potential biological activities. In this study, four valorization strategies for *S. muticum* biomass were compared under a life cycle perspective. Depending on the alternative, three products were obtained: sodiumalginate, antioxidant extract and fucoxanthin-containing extract. Regardless of the approach, the combined extraction of alginate and antioxidant from wet algae constituted the most efficient scenario. Among the stages, supercritical extraction of fucoxanthin and non-isothermal autohydrolysis were identified as the major environmental burdens due to electricity consumption. Although changes in product distribution fairly affected the environmental impacts of the scenarios, the single extraction of antioxidant fraction and the integral valorization to obtain fucoxanthin, alginate and antioxidant were only competitive when considering a functional unit based on the value of the products through an economic allocation approach instead of the amount of valorized algae.

Keywords Antioxidant, alginate, fucoxanthin, life cycle assessment, invasive macroalgae

1 Introduction

Invasive macroalgae are currently considered a major threat to native species and ocean’s resources worldwide (Schaffelke et al., 2006). The introduction of non-indigenous species may affect the existing habitats due to shifts in communities and trophic chains, which results in the decline of biodiversity and the alteration of the ecological stability of invaded ecosystems (Walker and Kendrick, 1998). Although biological invasion takes place naturally, anthropological activities such as heavy naval traffic, import of shellfish products or aquaculture have sharply accelerated this process and made it more frequent in both terrestrial and marine ecosystems over the last decades (Anderson, 2007; Schaffelke et al., 2006; Walker and Kendrick, 1998). Therefore, different strategies have been studied in order to control and prevent the proliferation of invasive species with different outcomes, essentially based on several mechanical removal procedures, but even considering the use of heat, chemicals (copper, chlorine, salt) or biological control by herbivorous mollusks (Anderson, 2007).

Sargassum muticum (Yendo) Fensholt is an invasive brown seaweed native to Japan which was introduced in North America by 1940s and in Europe during 1970s (Kraan, 2008; Walker and Kendrick, 1998). Nowadays, due to its extensive reproductive capacity, *S. muticum* is almost worldwide distributed, including different areas of the Pacific coast from Alaska to Mexico, the North Sea (Belgium, Denmark, the Netherlands...), major areas in Portugal, Spain, France and Ireland, as well as the English Channel coast or the Mediterranean Sea (Davis et al., 2004;

Kraan, 2008). Moreover, several studies have already highlighted the effect that *S. muticum* has on native communities (Britton-Simmons, 2004; Kraan, 2008). Although the influence on other species is limited in the foreshore, native populations are strongly affected by the organism according to studies in the subtidal zone (deepest area of the shore), probably related to shading effects (Britton-Simmons, 2004).

Due to the ecological problems caused by Sargassum sp, seasonal harvesting appears as an alternative to control algae proliferation (Kraan, 2008). Nevertheless, this measure entails the accumulation of large quantities of biomass that needs to be treated or utilized for valuable applications. The potential valorization of the resulting biomass lies in the capability of Sargassum sp to produce numerous high-value compounds with potential pharmaceutical applications. Particularly *S. muticum* exhibits a significant amount of phenolic compounds with biological activities, such as antifouling or antioxidant properties (González-López et al., 2012; Plouguerné et al., 2010). In addition, the seaweed contains polysaccharides, namely alginate and fucoidans, which justify its widespread use for metal biosorption (Davis et al., 2004), but also make it a good candidate in food, pharmaceutical or cosmetics sectors due to properties such as antioxidant, anticoagulant, antithrombic, antitumor and antiviral activities (Balboa et al., 2013).

Moreover, *S. muticum* also contains low amounts of the xanthophyll fucoxanthin, a yellowish pigment with promising applications based on its antioxidant, anti-inflammatory, anticancer, anti-obese, antidiabetic and antiangiogenic activities, as well as protective effect in several organs (Balboa et al., 2013; Conde et al., 2012).

The use of these functional compounds from macroalgae requires the selection of a suitable extraction method, according to several criteria such as selectivity, cost-effectiveness and environmental performance (Kadam et al., 2013). Regarding phenolic compounds, the total content and its antioxidant activity is highly dependent on the chosen method (Kadam et al., 2013). Solvent extraction is the most widely used technique for this purpose, though it requires long extraction times as well as the use of aqueous organic solvents such as methanol, ethanol and acetone (García-Salas et al., 2010; Kadam et al., 2013). Therefore, alternative methods have been proposed such as supercritical fluid extraction, pressurized liquid extraction or ultrasound-assisted extraction (García-Salas et al., 2010). In the case of alginate, the standard extraction method consists of a neutral extraction by performing a pre-extraction with hydrochloric acid to obtain an alginic acid that is then neutralized by adding sodium hydroxide and finally precipitated with sodium chloride and ethanol. Other methods have also been applied with comparable results in terms of alginate yield, including alkaline extraction at room and high temperatures (Davis et al., 2004). With respect to polysaccharides, traditional techniques are also time-consuming and require large amounts of organic solvents for precipitation, so more recent methods for separation include novel technologies such as supercritical extraction, ultrasonic-assisted extraction and membrane separation (Ye et al., 2008). Organic solvent extraction is again the most frequent method to separate fucoxanthin from seaweeds, with methanol, ethanol or acetone as common solvents (Conde et al., 2012). However, apart from the aforementioned environmental problems, in this case solvents can damage the functional properties of the extract, so supercritical fluid extraction has been suggested as a more selective technology that allows obtaining an extract with fewer polar impurities and, therefore, an easier subsequent purification procedure (Conde et al., 2012).

In this study, the processing scheme described by González-López et al. (2012) as well as three additional configurations based on modifications of the first approach were evaluated from an environmental perspective with the aim of identifying the most suitable valorization route.

The process consisted of consecutive extraction stages of the valuable biologically active compounds (fucoxanthin-containing extract by supercritical fluid extraction, alginate by alkaline extraction and antioxidant extract by non-isothermal autohydrolysis) to achieve an integral utilization of *S. muticum*.

Life Cycle Assessment (LCA) standardized methodology was used to evaluate the environmental aspects and potential impacts of the process (ISO 14040, 2006). This methodology has already been applied in a small number of studies related to the potential of macroalgal biomass as a feedstock in the production of biogas and bioethanol (Alvarado-Morales et al., 2013; Aresta et al., 2005). Although the production of high value bioactive molecules from other marine sources has also been evaluated through a LCA perspective (Pérez-López et al., 2014), there are no available studies focused on the production of these biocompounds from macroalgae harvested from nature.

2 Methods

2.1 Goal and scope definition

This study aims at identifying the environmental profile associated with the valorization of the invasive macroalgae *S. muticum* in four different scenarios. The main goal is to determine the most sustainable route, from an environmental point of view, to utilize *S. muticum* biomass. The compared processes were evaluated according to a cradle to gate perspective, including the production of the different inputs to the system, as well as the harvesting of macroalgal biomass, cleaning and preparation of the harvested biomass and further extraction and purification. Depending on the selected alternative, three main products were obtained: sodium alginate, antioxidant extract and fucoxanthin-containing extract. Additionally, the remaining algal residue resulting from each process was considered as subproduct due to its potential use as fertilizer.

2.1.1. Functional unit

One of the key parameters to select when performing a LCA is the functional unit (FU) or reference value to which inputs and outputs to the system and environmental impacts are expressed. FU shall therefore reflect the function of the studied system and its choice strongly depends on the aim of the study (Schau and Fet, 2008). In this case, the purpose of the process was to valorize an existing biomass that otherwise would have to be treated as a waste. From this perspective, 1 kg of final valorized biomass was selected as the FU.

2.1.2. System boundaries

The system under study consisted of six main subsystems: harvesting of the macroalgae from the natural environment (S1), pretreatment for extraction (S2), supercritical extraction of fucoxanthin-containing extract (S3), extraction of alginate from the algal biomass (S4), precipitation of alginate (S5) and non-isothermal autohydrolysis to obtain the antioxidant extract (S6). Only subsystems S1, S2 and S6 were common to the four analyzed scenarios; whereas S3 was only performed when fucoxanthin-containing extract was one of the target products and S4 and S5 were not required in case alginate was not extracted. The subsystems and unit processes included within the system boundaries are depicted in **Figure 1** and described below.

2.1.2.1. Harvesting of the macroalgae from the natural environment (S1)

The collection was carried out by two methods consisting of (i) direct manual harvesting of macroalgae that arrived at the beach due to tides or (ii) collection from the sea by boat. The amount of biomass collected by each procedure was estimated as 20% by boat and 80% at the beach (Manuel Loureiro, Conservas y Ahumados Lou SL, March 2013, personal communication). The system boundaries include the materials and fuel, as well as emissions to environment associated with vessel operations for the collection. In addition, water to clean and rinse the collected biomass to remove impurities (sand, epiphytes...) was considered, as well as the use of polyethylene and nylon for nets.

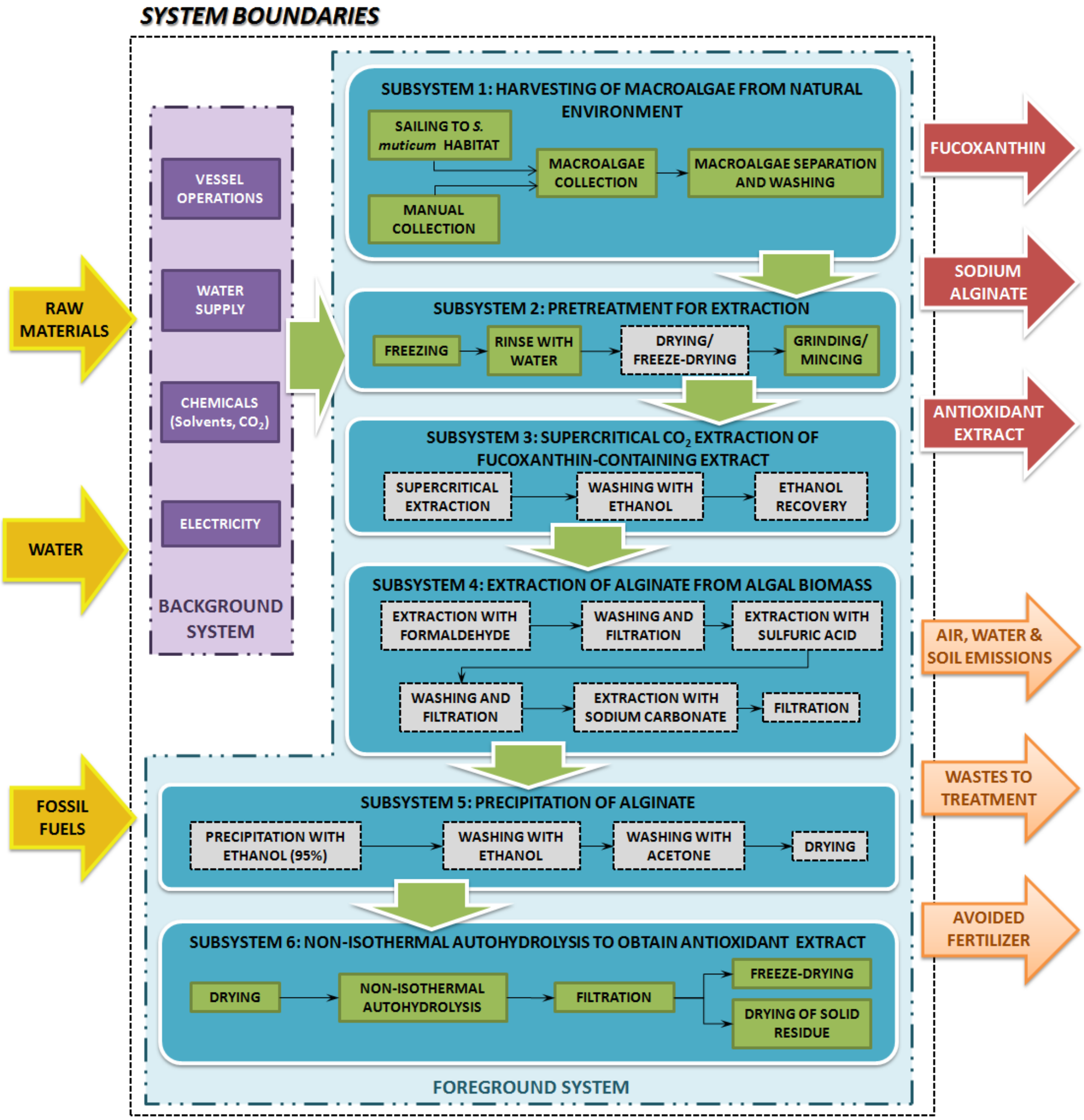

Figure 1 Process chain and system boundaries of the integral valorization of the macroalga *Sargassum muticum* by sequential extraction of fucoxanthin-containing extract, alginate and antioxidant extract (blocks in grey with discontinuous lines refer to steps that are not common to the four assessed scenarios).

2.1.2.2. Pretreatment for extraction (S2)

The clean biomass was kept in the freezer for a week (as average) before additional rinsing with water. The next stage depended on the considered scenario: in the base scenario (Sc 1), the algal biomass was dried in oven for 2 h before grinding it for 1 h. This stage was initially proposed since some algal canning factories use this procedure to process algae for food uses. This option would facilitate room storage of algae. Experimental work showed the possibility to perform the extractions with wet algae, so drying stage was not considered in Sc 2 and Sc 3, and grinding was substituted by mincing. Finally, when carrying out the supercritical extraction before alginate and antioxidant extractions (Sc 4), biomass had to be previously freeze-dried and ground.

2.1.2.3. Supercritical extraction of fucoxanthin-containing extract (S3)

This subsystem is only included in Sc 4. In this scenario, a limited portion of the fucoxanthin contained in the biomass (12 mg from a total of 55.1 mg fucoxanthin per 100 g dry weight macroalgal biomass) was separated through supercritical CO_2 extraction (P = 20–40 MPa and T = 40–55°C; 140 kg CO2/kg valorized biomass with no recycling system), using ethanol as co-solvent (21 L/kg valorized algae with no recovery system) and operating the system for 1 h. In this case, 90% recovery and reuse of both CO_2 and ethanol were assumed. The obtained extract contained 5–10% fucoxanthin.

2.1.2.4. Extraction of alginate from algal biomass (S4)

In all scenarios except for Sc 3, the remaining algal biomass was then extracted at room temperature with consecutive additions of formaldehyde 1% (15 h), sulfuric acid 0.2 N (4 h) and sodium carbonate 1% (15 h) in a sequential process with intermediate filtrations and washings of solids using distilled water. Stirring in all the extractions was also included within the system boundaries.

2.1.2.5. Precipitation of alginate (S5)

Once the liquid fraction containing sodium alginate (11.4% algal biomass in dry weight) was separated, a precipitation process was performed. The process consisted of the addition of ethanol 95% (15 min stirring, 1 h resting) and a washing step with absolute ethanol and acetone, followed by a drying step in oven. A solvent recovery of 90% was assumed for ethanol (total consumption of 106 L/kg valorized algae with no recovery system), whereas no acetone recovery was considered due to the low need for this solvent (8 L/kg valorized algae).

2.1.2.6. Non-isothermal autohydrolysis to obtain antioxidant extract (S5)

The solid fraction obtained after the last filtration in S4 (or after mincing in S2 for Sc 3) was rich in antioxidant extract. In the four scenarios, this solid was dried for two days in an oven at 50°C and treated with water in a batch reactor under non-isothermal conditions (final temperature of 170°C, which renders to the maximum content in fucoidans within the extract that corresponds

to 20–30% of the product) at a liquid/solid ratio of 60:1 g g_1. Once the selected temperature was reached, the biomass was kept in the reactor for 30 min and then cooled to 50–60°C and opened. The antioxidant extract (21% algal biomass in dry weight) was recovered by filtration and freeze-dried, whereas the algal paste with potential use as fertilizer was dried in oven for two days.

2.1.3. Evaluated scenarios

The evaluated extraction routes, schematized in **Figure 2**, were:

- Scenario 1 (Sc 1): Base scenario described by González-López et al. (2012), consisting of the valorization of dry algal biomass by alkaline extraction and precipitation of alginate followed by a non-isothermal autohydrolysis to separate an antioxidant extract rich in phenolics and polysaccharides, with potential applications in cosmetics industry.
- Scenario 2 (Sc 2): Valorization of wet algal biomass by alkaline extraction and precipitation of alginate followed by a non-isothermal autohydrolysis to separate the antioxidant extract.
- Scenario 3 (Sc 3): Valorization of wet algal biomass by non-isothermal autohydrolysis to obtain the antioxidant extract.
- Scenario 4 (Sc 4): Integral valorization of freeze-dried algal biomass based on the supercritical fluid extraction of fucoxanthin-containing extract followed by alkaline extraction and precipitation of alginate as well as non-isothermal autohydrolysis to obtain the antioxidant extract.

The protocols for the different alternatives of separation and purification were developed by the Group EQ2 of Chemical Engineering (www.grupoeq2.es) in the Faculty of Sciences in Ourense, at the University of Vigo (Spain).

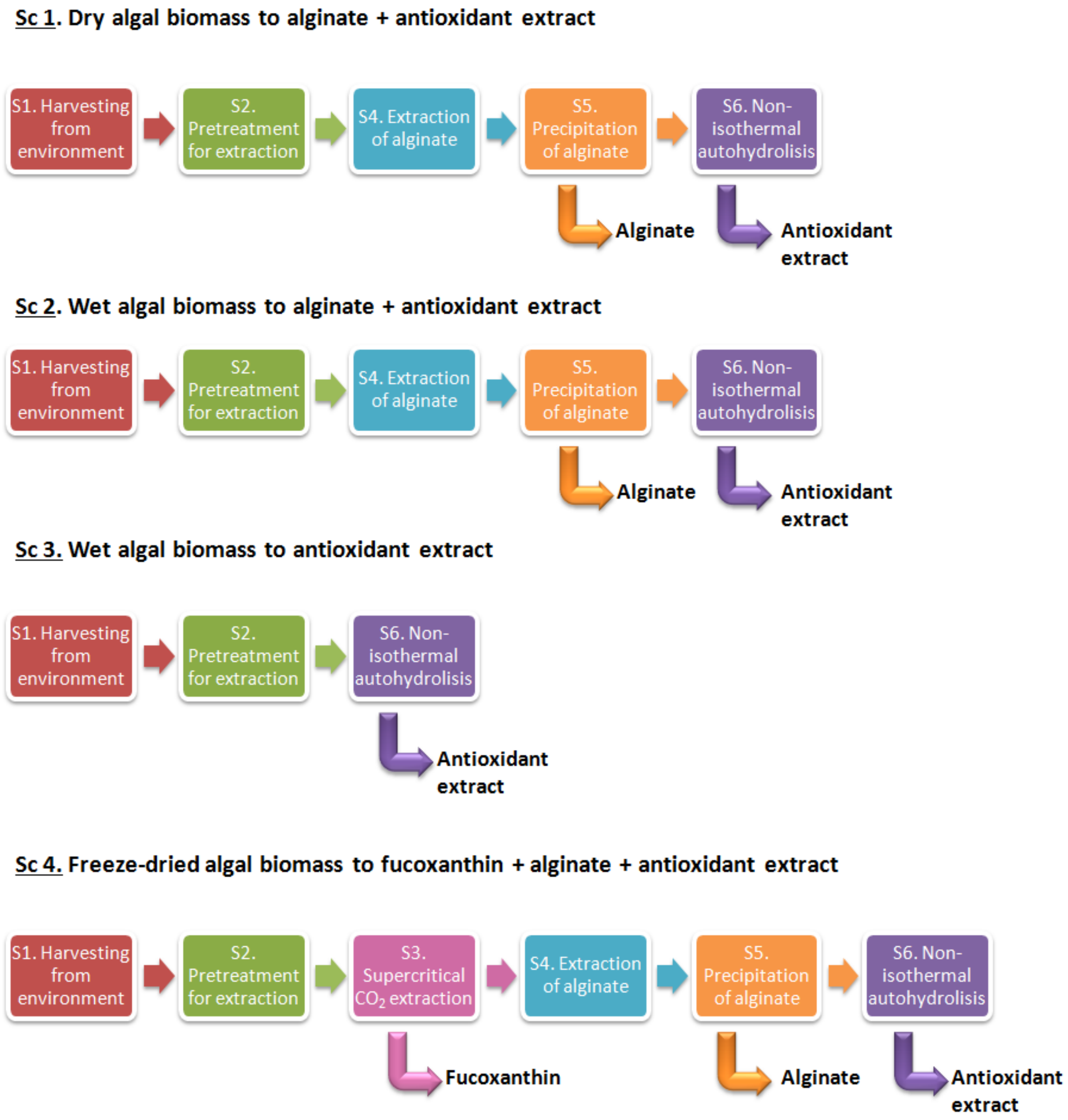

Figure 2 Schematic view of the stages performed and products obtained in each of the compared scenarios.

2.2 Inventory analysis, data quality and assumptions

Life Cycle Inventory (LCI) stage requires the collection of high quality data, which are essential for a reliable assessment. In this case, foreground data for the six subsystems were collected from different sources and procedures, as indicated in **Table 1**.

Table 1 Summary of data sources for foreground system.

Subsystem	Data required	Data sources
S1. Collection from natural environment	Polyester	Manufacturers' specifications, personal communication, Hospido and Tyedmers (2005).
	Steel	
	Antifouling	Manufacturers' specifications, Vázquez-Rowe et al (2010).
	Paint	
	Lubricant oil	
	Tap water	Personal communication, according to consumption at canning facility.
	Polyethylene (LDPE)	Experimental data, on-site measurement.
	Nylon	
	Emissions	Estimated according to Vázquez-Rowe et al (2010), Hospido and Tyedmers (2005).
	Wastes to treatment	Calculated from mass balances.
S2. Pretreatment for extraction	Tap water	Experimental data, on-site measurement.
	Electricity consumption	Estimated from power of equipment and duration of stage.
	Emissions	Calculated from mass balances.
S3. Supercritical extraction of fucoxanthin-containing extract	Ethanol	Experimental data, on-site measurement. Assumed recovery or recirculation.
	Carbon dioxide	
	Electricity consumption	Estimated from power of equipment and duration of stage.
	Emissions	Calculated from mass balances.
S4. Separation of alginate from antioxidant fraction	Tap water	Experimental data, on-site measurements. Gonzalez-López et al. (2012).
	Distilled water	
	Formaldehyde	
	Sulfuric acid	
	Disodium carbonate	
	Electricity consumption	Estimated from power of equipment and duration of stage.
	Emissions	Calculated from mass balances.
S5. Precipitation of alginate	Ethanol	Experimental data, on-site measurements. Gonzalez-López et al. (2012).
	Acetone	
	Distilled water	
	Electricity consumption	Estimated from power of equipment and duration of stage.
	Emissions	Calculated from mass balances.
S6. Non isothermal autohydrolysis to obtain antioxidant extract	Distilled water	Experimental data, on-site measurements.
	Electricity consumption	Estimated from power of equipment and duration of stage.
	Emissions	Calculated from mass balances.

The inputs for the collection of biomass from natural environment (S1), including fuel consumption, as well as materials of the vessel and chemicals associated with maintenance, were obtained from manufacturers' specifications and personal communications with expert advisors.

Materials for the vessel were estimated according to average dimensions and weights. A shared used of the boat was considered (1600 h per year) and three months of operation were considered associated with the seasonal harvest of the macroalgae (480 h). Materials for hull and engine were increased by 25% and 50% respectively, and life spans of 30 and 15 years were considered, according to Hospido and Tyedmers (2005). Chemicals related to vessel operations (i.e. paint, antifouling paint, marine lubricant oil), as well as water and air emissions from fuel combustion discharged to the environment were inventoried according to Vázquez-Rowe et al. (2010), considering manufacturers' specifications. For paint and anti-fouling emitted to marine environment, a loss of two thirds of the total amount used was considered (Hospido and Tyedmers, 2005).

For the next subsystems (S2 to S6), chemicals and water consumptions were estimated from experimental data obtained by on-site measurements and completed with information from González-López et al. (2012). Electricity consumptions were extrapolated on the basis of the power of the equipment, processing capacity and duration of each stage. As the inventory is associated with a hypothetical facility placed in shore, transport of equipments and chemicals was considered negligible. Water and air emissions were calculated on the hypothesis that the chemicals which are not consumed during the process are directly discharged.

Concerning the background system, the corresponding inventory data for the production of all the inputs to the system were taken from Ecoinvent database. These inputs included the production of chemicals required for the extraction stages, the production of electricity used within the stages of the process, as well as the materials for the vessel needed for the algae collection and waste disposal. A detailed description of the corresponding database reports considered is shown in **Table 2**.

Table 2 Summary of data sources for background system

Energy	Diesel	Ecoinvent database (Jungbluth 2007)
	Electricity (Spanish electricity profile)	Ecoinvent database (Dones et al. 2007)
Chemicals related to vessel operation	Anti-fouling	Vázquez-Rowe et al. (2010)
	Boat paint	
	Marine lubricant oil	
Materials for collection from natural environment	Glass fibre reinforced plastic, polyester resin	Ecoinvent database (Kellenberger et al 2007)
	Steel	Ecoinvent database (Classen et al. 2007)
	Polyethylene	Ecoinvent database (Hischier 2007)
	Nylon	
Chemicals	Formaldehyde	Ecoinvent database (Althaus et al. 2007)
	Sulfuric acid	
	Acetone	
	Carbon dioxide	
	Sodium carbonate	Ecoinvent database (Sutter 2007a)
	Ethanol	Ecoinvent database (Sutter 2007b)
Water supply	Tap water	Ecoinvent database (Althaus et al. 2007)
	Distilled water	
Waste treatment	Inert landfill	Ecoinvent database (Doka 2007)
	Sanitary landfill	
	Municipal incineration	
Avoided product: fertilizer	Ammonium sulfate	Ecoinvent database (Nemecek and Kägi 2007)
	Municipal incineration	

Finally, all the scenarios allow obtaining a biomass residue with potential applications as fertilizer. To do so, the content in carbon and nitrogen, as well as the ratio C/N were determined. The measured content of carbon was 45.6 ± 0.2% (dry weight) and the content of nitrogen was 1.5 ± 0.2% (dry weight). Since the obtained C/N ratio is higher than 25, all the nitrogen present in the residual biomass can be uptaken by the plants. Once the fertilizer potential was estimated, the equivalent amount of a typical fertilizer (containing ammonium sulfate as N source) was considered in the model as avoided product, which resulted in negative impacts that were subtracted from the environmental burdens.

The global inventory of the four assessed scenarios is shown in **Table 3**. According to the selected FU (1 kg valorized algae), no allocation procedure was required.

Table 3. Global inventory table for the valorization of invasive macroalga *S. muticum* (FU: 1 kg valorized biomass)

INPUTS from TECHNOSPHERE				
	Sc 1. Alginate + antioxidant extract from dry alga	Sc 2. Alginate + antioxidant extract from wet alga	Sc 3. Antioxidant extract from wet alga	Sc 4. Fucoxanthin-containing extract + alginate+ antioxidant extract from freeze-dried alga
Materials				
Polyester	65.37 g		101.13 g	65.34 g
Steel	19.61 g		30.34 g	19.60 g
Antifouling	41.61 g		64.37 g	41.59 g
Paint	10.47 g		16.19 g	10.46 g
Lubricant oil	51.92 g		80.33 g	51.91 g
Tap water	260.82 kg		403.50 kg	260.72 kg
Polyethylene (LDPE)	32.23 g		49.86 g	32.22 g
Nylon	17.75 g		27.45 g	17.74 g
Tap water	1219.03 kg		259.40 kg	1218.58 kg
Carbon dioxide	0		0	45.15 kg
Ethanol	39.64 kg		0	106.70 kg
Distilled water	644.58 kg		288.217 kg	646.23 kg
Formaldehyde	1.43 kg		0	1.43 kg
Sulfuric acid	1.74 kg		0	1.74 kg
Disodium carbonate	1.75 kg		0	1.75 kg
Acetone	20.79 kg		0	20.78 kg
Energy				
Diesel (associated with S1. Collection from natural environment)	23.25 kg	23.25 kg	35.97 kg	23.24 kg
Electricity from the grid (used in all the stages except for S1)	1075.05 kWh	931.46 kWh	1586.00 kWh	3207.02 kWh
INPUTS from ENVIRONMENT				
Materials				
Macroalgal biomass	3.11 kg$_{DW}$		4.81 kg$_{DW}$	3.11 kg$_{DW}$
Sand and residues	155.25 g		240.18 g	155.19 g
Seawater	29.42 kg		45.52 kg	29.41 kg
OUTPUTS to TECHNOSPHERE				
Products				
Fucoxanthin	0		0	0.37 g
Alginate	0.35 kg		0	0.35 kg
Antioxidant extract	0.65 kg		1.00 kg	0.65 kg
Avoided product[1]				
Nitrogen-rich fertilizer (expressed as kg N)	8.10 g		12.53 g	8.10 g

Table 3. Global inventory table for the valorization of invasive macroalga *S. muticum* (FU: 1 kg valorized biomass) (Cont.).

	Sc 1. Alginate + antioxidant extract from dry alga	Sc 2. Alginate + antioxidant extract from wet alga	Sc 3. Antioxidant extract from wet alga	Sc 4. Fucoxanthin-containing extract + alginate+ antioxidant extract from freeze-dried alga
OUTPUTS to TECHNOSPHERE				
Wastes to landfill				
Polyester, to sanitary landfill	65.37 g		101.13 g	65.34 g
Steel, to inert landfill	19.61 g		30.34 g	19.60 g
Polyethylene, to sanitary landfill	32.23 g		49.86 g	32.22 g
Nylon, textiles to municipal incineration	17.75 g		27.45 g	17.74 g
OUTPUTS to ENVIRONMENT				
Water emissions				
Xylene	3.71 g		5.748 g	3.71 g
Cobalt	1.59 mg		2.46 mg	1.59 mg
Copper	8.62 g		13.34 g	8.62 g
Zinc	3.90 g		6.03 g	3.90 g
Ethylbenzene	0.97 g		1.50 g	0.97 g
Sea nine 211	0.42 g		0.64 g	0.42 g
4-methylpentan-2-one	0.42 g		0.64 g	0.42 g
Wastewater	2125.67 kg		989.53 kg	2126.75 kg
Ethanol	39.91 kg		0	106.98 kg
Formaldehyde	1.43 kg		0	1.43 kg
Sulfuric acid	1.74 kg		0	1.74 kg
Acetone	20.79 kg		0	20.78 kg
Disodium carbonate	1.75 kg		0	1.75 kg
Air emissions				
Carbon dioxide	73.65 kg		113.94 kg	73.62 kg
Sulfur dioxide	0.05 kg		0.07 kg	0.05 kg
Non-methane volatile organic compounds (NMVOC)	0.69 kg		1.06 kg	0.69 kg
Methane	4.19 kg		6.47 kg	4.18 kg
Nitrogen oxides (NOx)	0.55 kg		0.84 kg	0.55 kg
Carbon monoxide	0.17 kg		0.27 kg	0.17 kg
Particulates	0.04 kg		0.07 kg	0.04 kg
Carbon dioxide	73.65 kg		113.94 kg	118.79 kg

[1] N dosage is equivalent to 1.5% (dry weight) nitrogen content within biomass. Since C/N ratio is higher than 25, all present nitrogen can be absorbed by plants.

2.3 Life cycle impact assessment

Among the phases defined by LCA standard methodology (ISO 14040, 2006) only classification and characterization stages were undertaken, since normalization and weighting are optional (and, to some extent, subjective) elements that provide no additional information according to the goal and scope of the study.

Characterization factors reported by the Centre of Environmental Science of Leiden University (CML 2001 method) were applied (Guinée et al., 2002), and the potential impact categories analysed were: abiotic depletion (ADP), acidification (AP), eutrophication (EP), global warming (GWP), ozone layer depletion (ODP), human toxicity (HTP), freshwater aquatic ecotoxicity (FEP), marine aquatic ecotoxicity (MEP), terrestrial ecotoxicity (TEP) and photochemical oxidants formation (POFP).

3 Results and discussion

3.1 Comparative environmental performance of the valorization strategies of S. muticum biomass

LCA characterization results of the evaluated scenarios are summarized in **Table 4** and calculated taken 1 kg of valorized biomass as reference. According to the results depicted in **Figure 3**, valorization by extracting sodium alginate and antioxidant fraction from wet algae would be the most appropriate route in terms of most impact categories. Thus, Sc 2 presents contributions between 4% (for FEP) and 12% (for EP, MEP or TEP) lower than the impacts of the base scenario Sc1. Moreover, the environmental profiles of strategies Sc 1 and Sc 2 are also better than the performance of Sc 3. Thus, the contributions when extracting only the antioxidant fraction are from 14% to 44% higher than those of Sc 1 and exceed the values of Sc 2 in a range of 26% up to 64%, except for FEP that presents a contribution 52% lower than Sc 1 and 49% lower than Sc 2. Finally, Sc 4 was found as the alternative with the highest contributions in all the evaluated categories, being these contributions more than 1.5 times higher for FEP and nearly 3 times higher for HTP, MEP or TEP in comparison with the other three scenarios.

Table 4. Impact assessment results (characterization step) associated with 1 kg valorized *Sargassum muticum* in the four evaluated scenarios.

Impact category	**Unit**	**FU: 1 kg valorized *Sargassum muticum***			
		Sc 1	**Sc 2**	**Sc 3**	**Sc 4**
Abiotic depletion (ADP)	kg Sb $_{eq}$	6.73	6.11	7.70	17.54
Acidification (AP)	kg $SO_{2\ eq}$	8.13	7.31	9.75	20.58
Eutrophication (EP)	kg $PO_4{}^{-3}{}_{eq}$	1.43	1.27	1.97	4.05
Global warming (GWP)	kg $CO_{2\ eq}$	917.47	832.56	1220.82	2341.76
Ozone layer depletion (ODP)	mg CFC-11 $_{eq}$	47.40	42.82	67.52	120.03
Human toxicity (HTP)	kg 1,4-dichlorobenzene (DB_{eq})	197.12	173.14	274.74	602.29
Freshwater aquatic ecotoxicity (FEP)	kg 1,4-DB_{eq}	605.06	578.95	292.88	1007.06
Marine aquatic ecotoxicity (MEP)	kg 1,4-DB_{eq}	131.14	114.61	188.37	385.95
Terrestrial aquatic ecotoxicity (TEP)	g 1,4-DB_{eq}	45.23	39.84	61.61	128.10
Photochemical oxidants formation (POFP)	g $C_2H_{4\ eq}$	333.42	303.55	392.28	880.84

Sc 1. Alginate + antioxidant extract from dry alga

Sc 2. Alginate + antioxidant extract from wet alga

Sc 3. Antioxidant extract from wet alga

Sc 4. Fucoxanthin-containing extract + alginate + antioxidant extract from freeze-dry alga

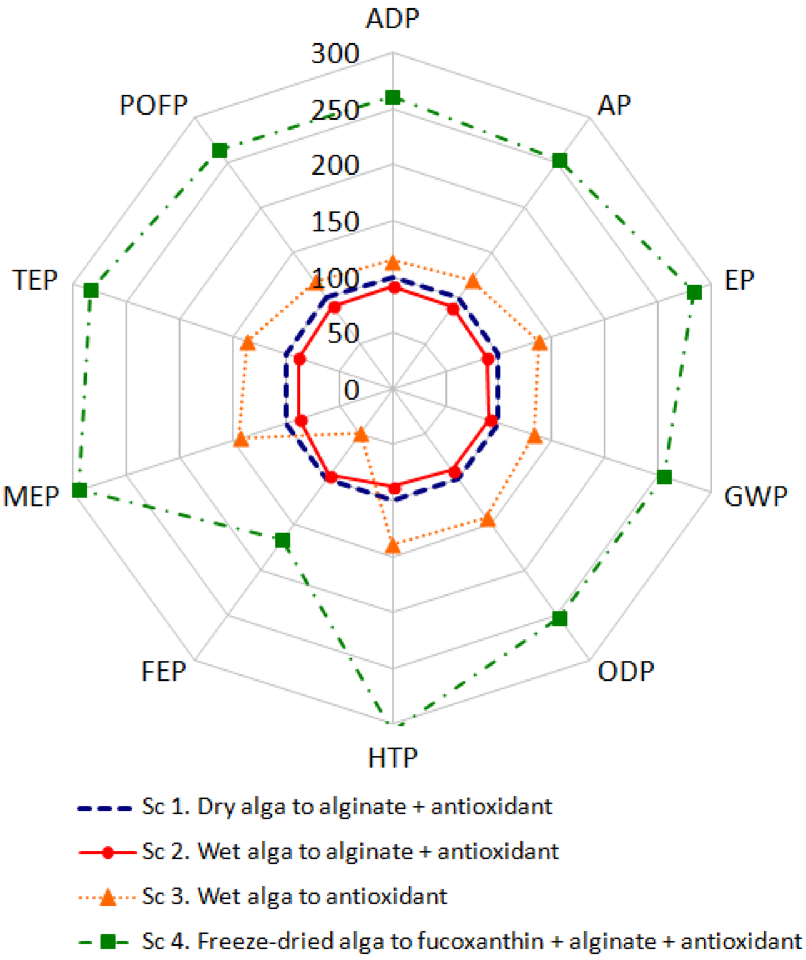

Figure 3. Relative environmental profile of the compared valorization scenarios with Sc 1 being the baseline (index=100) when considering 1 kg valorized alga as functional unit.

3.2 Identification of hot spots for the valorization strategies of *S. muticum* biomass

Figure 4 depicts the most problematic subsystems contributing to the environmental impacts of the four valorization alternatives. In the case of Sc 1, the non-isothermal hydrolysis (S6) is the major contributor to most impact categories that accounts from 45% up to 60%, except for FEP, which is dominated by the extraction of alginate from the algal biomass (S4) with 70% of the contribution. S4 also has a significant effect in terms of AP (21%). Among the secondary stages, the pretreatment of algal biomass for extraction (S2) has remarkable contributions, especially in

EP (21%), HTP (22%), MEP (23%) and TEP (22%). The collection of algae from natural environment (S1) is responsible for 20% of impact to GWP and nearly 23% ODP, whereas the precipitation of alginate (S5) has rather limited effects in most categories, despite being the second cause of ADP (22%) and POFP (20%).

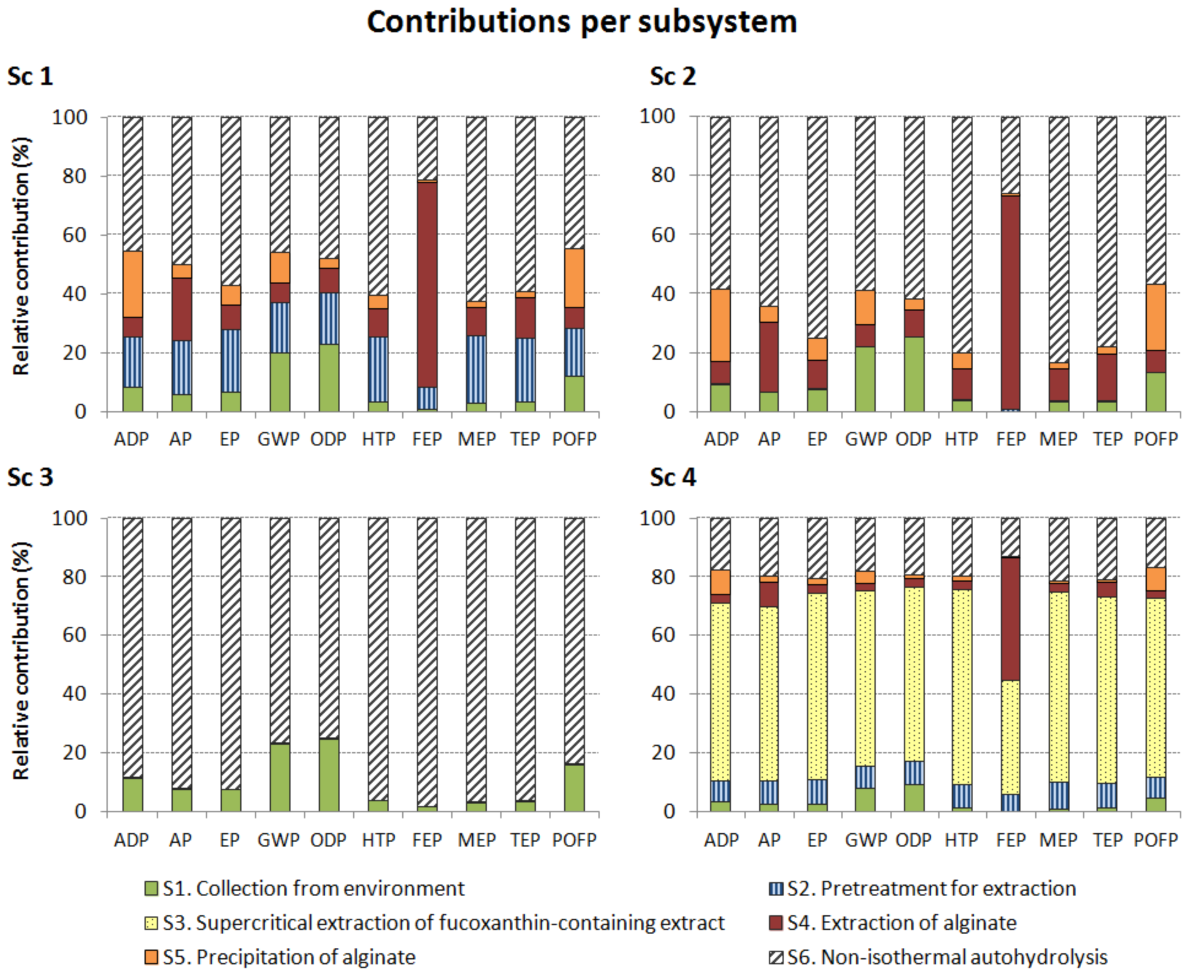

Figure 4. Relative contributions per subsystem to the environmental profile of the compared scenarios for 1 kg valorized alga as functional unit.

Regarding the activities associated with these impacts, shown in **Figure 5**, electricity is clearly the hot spot in Sc 1. This activity exhibits a global contribution ranging from 67% to 95% of the total impacts in all the categories except for FEP, which presents 66% of the impact related to waste streams (specifically linked to organic solvent emissions to water in S4). The highest electricity consumption (66% of total electricity) corresponds to S6 that has three energy-intensive steps with significant electricity requirements (drying, autohydrolysis in reactor itself and, to a larger extent, freeze-drying of the obtained extract), followed by S2 (24% of total electricity) mainly due to drying step for the preparation of the algae for extraction. Among the secondary processes, the production of chemicals constitutes a major contributor in terms of ADP (23%) and POFP (21%) related to the production of ethanol and, to a lesser extent, acetone, both required for the precipitation of alginate in S5. Vessel operations cause 20% of the total impact in GWP and 23% of ODP, especially due to the consumption of diesel and the derived greenhouse gas emissions. Although the use of residual biomass as a fertilizer represents a reduction of impact (avoided synthetic fertilizer), the limited amount of material results in a negligible improvement, much lower than 1% of the total impacts in all the categories.

When it comes to Sc 2, the effect of S2 is remarkably lower than for Sc 1, falling from contributions between 16% and 23% in most categories to less than 0.5%. This change is due to the omission of the drying stage (resulting in a remarkable reduction in electricity consumption) that was proven to be feasible without affecting the extraction stages and yields in scenarios where only alginate and antioxidant extract were obtained. Therefore, S6 dominates the environmental burdens (between 57% and 83% depending on the category) except for contributions to FEP, which are again associated with S4 (73% of total FEP). As in the previous case, S5 is only relevant for ADP (24%) and POFP (22%), whereas S1 affects GWP and ODP in 22% and 25% respectively. Concerning the production processes that are associated with the subsystems, the production of electricity to meet the energy requirements is again the hot spot with contributions that range between 64% and 94% to all the categories excluding FEP (69%

from waste treatment processes), despite the slight decrease of the influence of electricity with respect to Sc 1. Nearly 90% of this electricity consumption is related to S6, due to the combined requirements associated with the steps of drying, autohydrolysis and mostly freeze-drying. Following the same trend as Sc 1, vessel operations are responsible for the second highest contributions to GWP (22%) and ODP (25%), while the production of chemicals only affects ADP (25%) and POFP (23%).

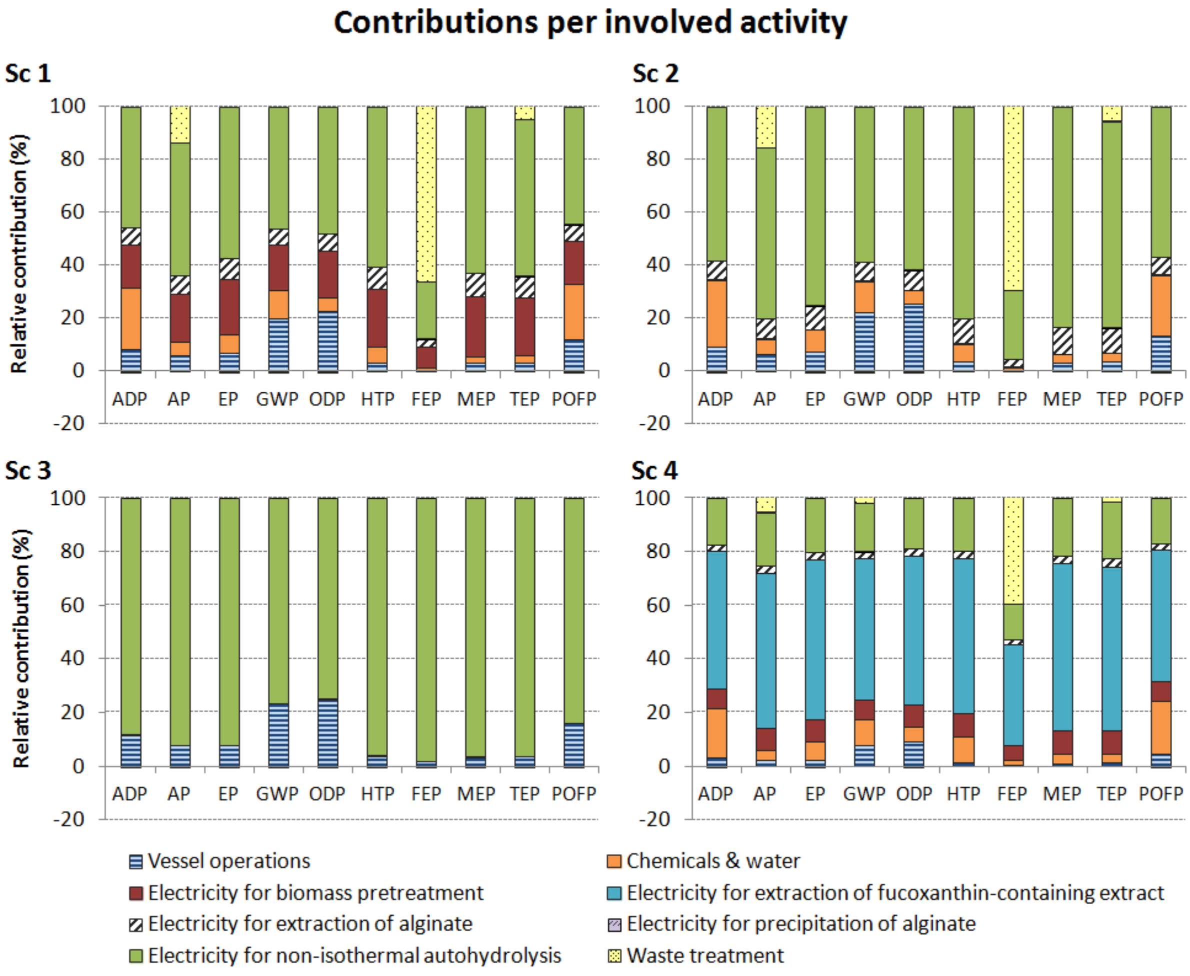

Figure 5. Relative contributions per involved activity to the environmental profile of the compared scenarios for 1 kg valorized alga as functional unit.

In the case of Sc 3, due to the elimination of S4 and S5, the contributions of S1 and S6 exhibit a noticeable increase in relative terms. S6 clearly constitutes the hot spot in all the evaluated categories, ranging from 75% to 98% of the impact depending on the category. S1 mainly affects GWP (23%) and ODP (25%). Regarding the involved activities, the contributions related to electricity are responsible for more than 75% of the impact to all categories, with 99% of these requirements coming from S6. Another significant change in this scenario is the sharp decrease of the impacts from waste treatment (from around 70% in Sc 1 and Sc 2 to 0.3% in Sc 3). This is due to the fact that no organic solvents are emitted to water when the extraction of alginate is not performed.

Finally, the environmental profile of Sc 4 is remarkably different compared with the other three situations as a result of the implementation of a supercritical extraction stage to obtain fucoxanthin-containing extract. In this case, S3 is certainly the major hot spot in all the impact categories with contributions between 39% and 66%. Among the other subsystems, S6 has significant effects in all categories (between 13% and 22%) and S4 only affects noticeably FEP (42%), while all the other contributions are below 10%. The main reason for this behavior is the need for electricity to satisfy the high energy requirements of the supercritical extraction that affect the impact categories between 38% and 62%. This consumption corresponds to 65% of the total electricity required, whereas more than 22% of the remaining demand is related to S6 and 9% is due to the freeze-drying of biomass in S2 that is necessary to perform the supercritical extraction. Among the processes that are not related to electricity, only three contributions exceed 10% of the impacts: the production of chemicals for ADP (18%) and POFP (20%), jointly with waste flows for FEP (40%).

3.3 Sensitivity assessment of the model

The comparative analysis conducted in this study shows up the great influence of the extraction pathway in the LCA results. Although no similar works related to valuable compounds obtained from macroalgae have been found in the literature, the identification of hot spots is consistent with previous findings related to the important effect of electricity requirements in harvesting and extraction processes associated with other products from marine organisms, such as lipid extraction from microalgae or biofuels from macroalgae (Aresta et al., 2005; Beach et al., 2012). Indeed, a 10% reduction in electricity requirements could lead to improvements between 3% and 10% of the total impacts depending on the considered category (Supplementary information, Fig. S1).

In addition to the impact associated with the production of electricity, organic solvents can also result in a significant contribution that in this case was observed when considering the precipitation of alginate. With this regard, Raymond et al. (2010) found that the possibility of solvent recovery or reduction could entail up to 90% of reduction in overall emissions. In this case, ethanol associated with alginate precipitation was the main contribution among the chemicals. As a recovery system was already taken into account or the base inventory, a comparison of the assessed scenarios with and without ethanol recovery was conducted (Supplementary information, Fig. S2). According to the results, solvent recovery is a key issue in the three scenarios that include the precipitation of alginate (Sc 1, Sc 2 and Sc 4). The omission of this system would cause a remarkable increase in the environmental impacts related to most categories, especially ADP and POPF, which exceed the original value in 25% for Sc 4 and nearly double their contributions when considering Sc 1 and Sc 2.

3.3.1 Effect of changes in biomass composition

The environmental results analyzed in the previous sections were calculated for the case in which the antioxidant extract contained the highest concentration of fucoidans (final temperature of 170°C during non-isothermal autohydrolysis). However, González-López et al. (2012) found a remarkable influence of the final heating temperature on the solubilization of solids and therefore, on the final amount of antioxidant extract obtained. As the antioxidant fraction constitutes the main product as much in mass as in economic terms, a change in the obtained amount may significantly affect the global environmental profile of the process. Moreover, the considered quantity of extracted fucoxanthin (12 mg fucoxanthin/100 g dry algae) corresponds to the maximum experimental yield obtained, although S. muticum contains up to 55.1 mg/100 g dry algae (Conde et al., 2012). Additionally, seasonal variations may also result in important changes in the composition of the biomass, and therefore in the product distribution (Balboa et al., 2013).

For this reason, a sensitivity assessment was conducted. The potential impacts for all the scenarios were calculated in two opposite situations: the maximization of the amount of antioxidant extract (autohydrolysis temperature of 200°C to obtain 41% dry algae as antioxidant extract) and the operation with minimum amount of antioxidant extract (temperature of 150°C to obtain 13% dry algae as antioxidant extract). For Sc 4, an additional situation was evaluated, considering the highest content of fucoxanthin in the biomass: 55.1 mg/100 g algae (Supplementary information, Tables S2–S5). The results reveal the clear dependence of the environmental performance on the operational conditions of S6. Thus, a change of 17% in the final temperature for the non-isothermal autohydrolysis (from 170 to 200°C) turns into a reduction of impact around 33% for Sc 1 and Sc 2, 44% for Sc 3 and 37% for Sc 4, whereas lowering temperature by 12% (from 170 to 150°C) involves increases from 25% (for Sc 1, Sc 2 and Sc 4) up to 50% for Sc 3. Concerning Sc 4, the increment in the recovered amount of fucoxanthin has virtually no effect in the environmental profile.

3.3.2. Effect of FU choice in the environmental profiles

The results from Sections 3.1 and 3.2 show that Sc 4 presents much higher environmental burdens than the other three alternatives. However, it should be pointed out that in this scenario an additional valuable compound is obtained. Fucoxanthin is a biologically active molecule with a high value, not only in economic terms, but also with potential uses in the pharmaceutical sector. Moreover, Sc 3 has higher environmental impacts than Sc 1 and Sc 2 in most categories per kg valorized biomass, but the obtained product (1 kg antioxidant extract) is significantly more valuable than the product of Sc 1 and Sc 2 (0.65 kg antioxidant extract and 0.35 kg alginate).

The obtained results are based on a FU that focuses on the amount of valorized biomass rather than on the obtained products. Indeed, the choice of the FU is a critical point in a LCA study and several authors consider it as a limitation since it is a subjective matter (Fleischer and Schmidt, 1996; Schau and Fet, 2008). The influence of the FU is particularly important when using LCA as a decision tool, so special attention must be paid to select an appropriate FU with an equivalent function in all the compared systems (Schau and Fet, 2008). The selected FU considers the maximization of valorized biomass as the main function of the system but does not include the benefits of the process associated with the production of valuable molecules.

Hence, a second approach is presented below, consisting of a FU focused on the products obtained instead of the amount of biomass processed. High-purity fucoxanthin has a market value of up to 9000 €/g, although the fucoxanthin-containing extract that is obtained in this case has a significantly lower price ranging between 40–240 €/g. The value of the antioxidant extract is estimated around 170 €/g (according to the price of similar extracts from other macroalgae) and that of sodium alginate is lower than 0.10 €/g (www.sigmaaldrich.com). Considering that the antioxidant extract and the alginate were the major components in quantitative terms and the antioxidant extract (obtained in all configurations) had a much higher value, the FU was selected as 1 kg of antioxidant extract. Since two additional co-products (fucoxanthin-containing extract and alginate) were obtained, economic allocation was applied according to the Handbook on Life Cycle Assessment (Guinée et al., 2002) and economic values of the three products were used for allocation. However, not all the subsystems were associated with the three products (e.g. supercritical extraction -S3- was only related to fucoxanthin), so allocation factors varied within the subsystems of each evaluated scenario. A summary of the considered allocation factors is given in **Table 5**.

The effect of this alternative FU in the environmental profiles is shown in **Table 6** and **Figure 6**. According to the considered economic allocation, the results change significantly with respect to the previous analysis. Thus, Sc 4 is not the alternative with the highest impacts and Sc 3 constitutes the least appealing option. However, the differences between scenarios 1, 3 and 4 are lower than 5% in all categories. The integral valorization of biomass by extracting the three high value compounds becomes competitive when considering the product-based FU with economic allocation. Again, Sc 2 is the preferred scenario according to the environmental performance and has contributions between 10% and 15% lower than Sc 1. The most relevant reductions of impact are linked to toxicity categories, because no solvents are needed to obtain the antioxidant extract.

Table 5. Partitioning fraction for economic allocation in the evaluated scenarios for 1 kg of antioxidant extract.

		g product/kg valorized alga	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 5**	**Stage 6**
Sc 1 and Sc 2	Fucoxanthin-containing extract	0	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
	Alginate	353.61	0.03%	0.03%	0.03%	100.00%	100.00%	0.00%
	Antioxidant extract	646.39	99.97%	99.97%	99.97%	0.00%	0.00%	100.00%
Sc 3	Fucoxanthin-containing extract	0	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
	Alginate	0	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
	Antioxidant extract	1000.00	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Sc 4	Fucoxanthin-containing extract	0.37	0.05%	0.05%	100.00%	0.00%	0.00%	0.00%
	Alginate	353.48	0.03%	0.03%	0.00%	100.00%	100.00%	0.00%
	Antioxidant extract	646.15	99.93%	99.93%	0.00%	0.00%	0.00%	100.00%

*Estimated market price of 140€/g for fucoxanthin-containing extract, 0.08 €/g for alginate and 167.30 €/g for antioxidant extract

Table 6. Impact assessment results (characterization step) associated with 1 kg antioxidant extract and two economic allocation approaches in the four evaluated scenarios.

Impact category	**Unit**	**FU: 1 kg antioxidant extract, approach a**				**FU: 1 kg antioxidant extract, approach b**			
		Sc 1	**Sc 2**	**Sc 3**	**Sc 4**	**Sc 1**	**Sc 2**	**Sc 3**	**Sc 4**
Abiotic depletion (ADP)	kg Sb_{eq}	7.36	6.41	7.70	7.66	8.09	7.14	7.70	8.39
Acidification (AP)	kg $\text{SO}_{2\ eq}$	9.31	8.05	9.75	9.70	11.99	10.73	9.75	12.34
Eutrophication (EP)	kg $\text{PO}_4^{-3}{}_{eq}$	1.88	1.63	1.97	1.96	2.07	1.82	1.97	2.15
Global warming (GWP)	kg $\text{CO}_{2\ eq}$	1174.86	1043.56	1220.82	1215.54	1271.19	1139.89	1220.82	1311.54
Ozone layer depletion (ODP)	mg CFC-11 $_{eq}$	64.98	57.89	67.52	67.18	71.00	63.91	67.52	73.17
Human toxicity (HTP)	kg 1,4-dichlorobenzene (DB_{eq})	261.77	224.70	274.74	273.29	290.58	253.50	274.74	301.69
Freshwater aquatic ecotoxicity (FEP)	kg 1,4-DB_{eq}	278.75	238.38	292.88	291.19	929.29	888.92	292.88	941.56
Marine aquatic ecotoxicity (MEP)	kg 1,4-DB_{eq}	179.43	153.88	188.37	187.32	198.64	173.09	188.37	206.42
Terrestrial aquatic ecotoxicity (TEP)	g 1,4-DB_{eq}	58.69	50.36	61.61	61.28	68.40	60.07	61.61	70.96
Photochemical oxidants formation (POFP)	g $\text{C}_2\text{H}_{4\ eq}$	376.13	329.94	392.28	390.46	410.72	364.53	392.28	423.35

Sc 1. Alginate + antioxidant extract from dry alga

Sc 2. Alginate + antioxidant extract from wet alga

Sc 3. Antioxidant extract from wet alga

Sc 4. Fucoxanthin-containing extract + alginate + antioxidant extract from freeze-dry alga

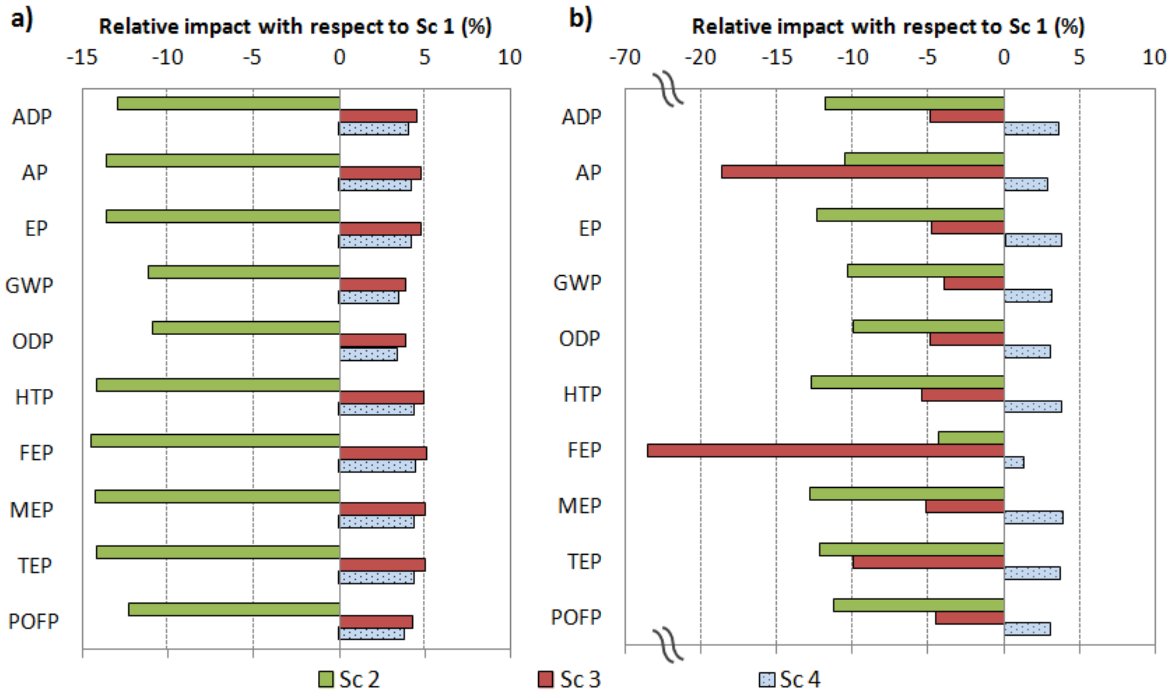

Figure 6. Relative environmental profile of Sc 2, Sc 3 and Sc 4 with respect to Sc 1 for 1 kg antioxidant extract as functional unit, with a) economic allocation considering null impact of antioxidant extract related to S4 and S5, and b) economic allocation considering benefits of S4 for antioxidant extraction due to biomass reduction.

These results are based on an economic allocation (a) that assigns a factor of 0 for the impact of the antioxidant extract related to S4 and S5, since these stages are not strictly necessary for obtaining the product. Nevertheless, the performance of stage S4 facilitates the non-isothermal autohydrolysis and allows reducing mass and energy consumptions in S6 due to the lower quantity of biomass treated. Therefore, a second allocation approach (b) was also assessed, allocating a fraction of the environmental main responsible for most impacts due, to a large extent, to the consumption of electricity in this stage. S2 has significant contributions in some specific categories, especially those related to toxicity, whereas the effect of S1 is limited to the categories of GWP, ODP and POFP, associated with vessel operations. S5 constitutes the main change with respect to the FU based on the valorized biomass, as it has no contribution to the impacts related to the antioxidant extract. S4 follows the same trend as S5 when considering approach a, although the behavior of this stage in economic allocation b is similar to the results of Section 3.2. Thus, in approach b S4 is the main responsible for impacts to FEP due to waste treatment associated with solvent residues.

4 Conclusions

The development of novel processes to valorize natural resources requires objective supporting tools to evaluate the efficiency of available technologies and identify the most suitable options from environmental, economic and social perspectives. Thus, the integral valorization of biomass, which was initially considered the most attractive scenario, is not necessarily a convenient approach. The results of this paper highlight the usefulness of LCA methodology as a decision-making tool, especially in processes under development related to emergent sectors such as marine biotechnology. The outcomes should be considered in order to improve current extraction techniques towards the optimal valorization of natural resources.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.03.013.

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