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Environmental life cycle assessment of biogas production from marine macroalgal feedstock for the substitution of energy crops

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ABSTRACT

The central objective of this paper is to evaluate the production of biogas by the substitution of energy crops with marine macroalgae: mixture of brown (20%) and red algae (80%) as feedstock in an industrial scale biogas plant. This plant operates with the co-digestion of maize (27%), grass (54%), rye (8%) and chicken manure (11) and produces 500 kWh energy. In order to assess environmental friendliness, a life cycle assessment was performed by using the software Simapro. Potential environmental impact categories under investigation were global warming, acidification, eutrophication and land transformation potential.

Our results determine the affirmative impact of the codigestion of algae with chicken manure on the emission reductions: 52%, 83%, 41% and 8% lower global warming, acidification, eutrophication and land transformation potentials, respectively per 1 MJ of energy generation, moreover, 84% and 6% lower acidification and land transformation potentials per kg of feedstock.

1. Introduction

Biomass resources are considered as one of the main renewable energy sources and expected to provide more than half of the energy demand in the near future (European Renewable Energy Council, 2008). Nevertheless, some studies suggest that intensive exploitation of arable land for the cultivation of energy crops may yield a negative impact on the global stock and prices of food and will lead to increasing quantities of greenhouse gases (GHG) being emitted to the atmosphere (Fargione et al., 2008; Johansson and Azar, 2007; Searchinger et al., 2008). For that reason, alternative sources of biomass for energy generation that would be both economically competitive and environmentally-friendly are required. Considering its high photosynthetic effectiveness, fast biomass growth and resistance to contaminations (heavy metals), algae appears as a competition to typical energy crops (Aitken et al., 2014; Alvarado-Morales et al., 2013; Lardon et al., 2009). Macroalgae has been harvested from the sea. Brown macroalgae dominate the harvest with twice the volume of red macroalgae. Green macroalgae (seaweed) are less valuable and are not harvested in significant amounts (Werner et al., 2004). According to Yokoyama et al. (2007), 0.9% of Japan's required CO_2 mitigation according to the Kyoto protocol could be achieved by farming macroalgae on a large scale. However, it has to be considered that burning or decomposing macroalgal biomass will only recycle carbon. In this respect, the application of macroalgae to produce energy appears to be a promising practice to complement energy supply based on biomass. This paper presents an assessment of the consequences for the sustainability of biogas production, when the energy crops are (partially) replaced with macroalgae (brown and red algae) as feedstock at an industrial scale biogas plant in Northeast Germany.

As macroalgae attracts quite a lot interest for biofuel production, this paper focuses on the macroalgae harvest from the regions or areas nearby the coast for biogas production and its replacement with energy crops. In many countries, an excessive natural growth of macroalgae has been observed as result of the progressive eutrophication of coastal water by excessive amount of N, P, CO_2 and insufficient amount of dissolved O_2. Macroalgae consume these nutrients for biomass growth. Collection of this biomass from beaches would result in clean beaches and altered impacts of eutrophication. This biomass could also represent a potential substrate in biogas plants as has recently been suggested by many authors (Allen et al., 2013; Bucholc et al., 2014). Current bioenergy projections are based on feedstock such as corn, soya bean and sugar cane, which are also food commodities. Energy and agricultural markets are closely linked, and due to their size the

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movements in energy markets affect agriculture more than vice versa. Therefore, algal biomass offers a number of advantages, especially the use of otherwise nonproductive land (in our case, no arable land use, due to harvest of beaches), and some others (Subhadra and Grinson, 2011). In case of integrated concepts, in which biogas production is coupled to a biorefinery concept, certain algae can be used for the production of other liquid and gaseous fuels like biohydrogen, see for a review e.g. (Kumar et al., 2015). Then, biomass residues of these processes might be used as feedstock for a final biogas production, before those are applied as fertilizer.

2. Methods

Life cycle assessment (LCA) is a method that evaluates the environmental impacts of a system by collecting an inventory data related to inputs and outputs. On the next step, it assesses the potential environmental effects of those inputs and outputs. As a last step; it interprets the results of the inventory and impact assessment based on the aim of the study (ISO, 2006). The standard ISO 14040:2006, which gives the basis for LCA procedures, was pursued in this study. The study analyses the Northeast region of Germany, which is characterized by sandy or loamy soil. The amount of rainfall is approx. 20% lower in comparison to other regions in Germany. That is why the inventory data, including the digestate composition, emissions, operation style of the biogas plant, agricultural management for crop cultivation, regional properties of the soil and climate conditions, are chosen to be descriptive for the area. The outcomes of this study may be further used for other geographical areas only after a suitable revision of data.

2.1. System boundary

Fig. 1 indicates both systems investigated: firstly the current production system with energy crops, and secondly, the alternative production system with the co-digestion of macroalgae and chicken manure. The analyzed systems involve the collection/production and storage of feedstock, anaerobic digestion, storage/handling of digestate, electricity and heat generation from biogas, and lastly the transportation.

2.2. Life cycle inventory analysis

Inventory Analysis is a stepwise methodology for measuring the energy and raw materials necessary, atmospheric and waterborne emissions, solid wastes, and other releases for the entire life cycle of the system. The inventories include all main process steps and contain resources used, as well as emissions to the air, water, or surrounding land until biomethane is released to the gas grid.

The amount of feedstock, biogas production and methane ratio, and electricity consumption were observed continuously at the plant during one year, in this case 2012. Material flows that could not be determined at the plant were calculated based on the assumptions from literature. The rest of the calculations were performed depending on the database of Ecoinvent 2.2 (the Ecoinvent Centre, Switzerland) (Hans-Jörg Althaus et al., 2010).

2.2.1. Determination of feedstock amounts/compositions and functional unit

The quantity of macroalgae to substitute energy crops was determined based on biogas yields. Characterization of feedstock, the total solid (TS), organic total solid (oTS) and the biogas yield

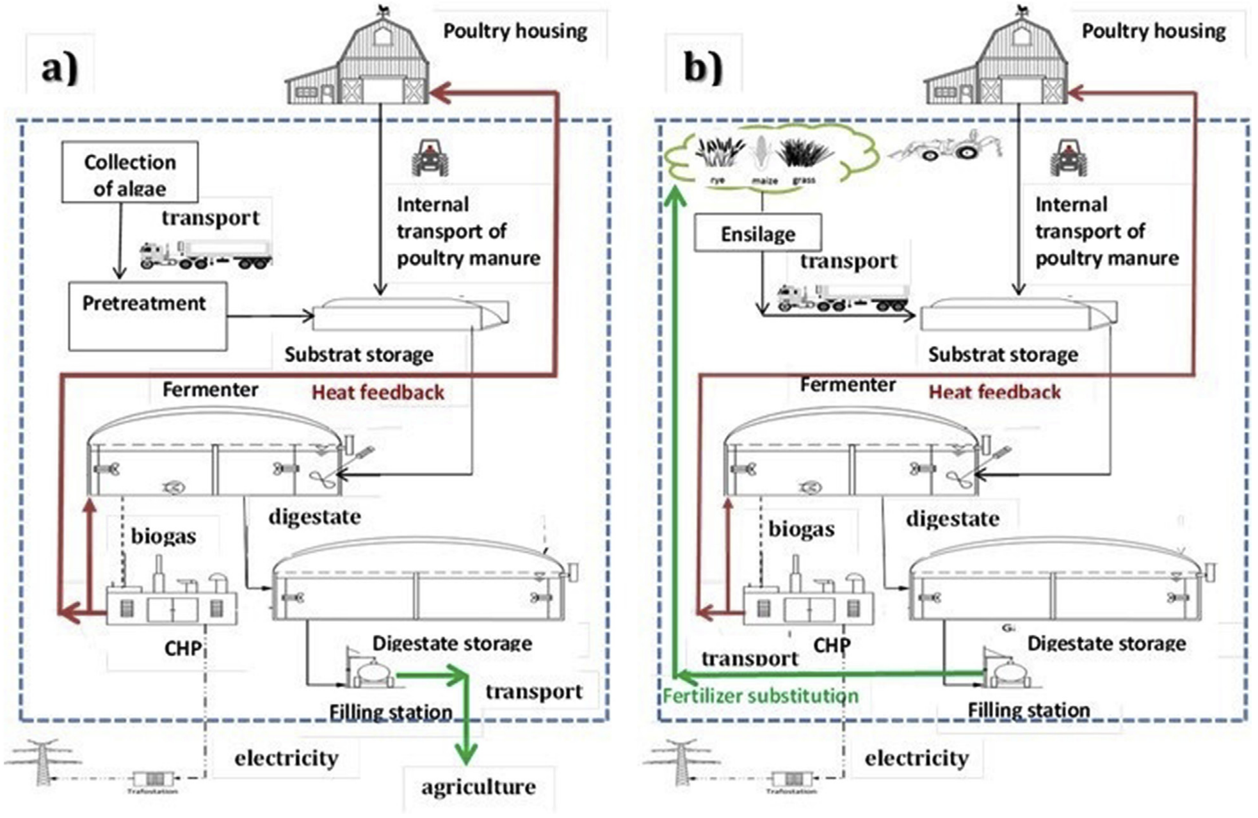

Fig. 1. System boundary: Energy production from the co-digestion of chicken manure with a) Macroalgae and b) Energy crops. Adapted from (KTBL, 2014). The arrows indicate material and energy flows.

Table 1
Characteristics of the feedstock.

Feedstock	Macroalgae	Maize silage	Rye silage	Grass silage	Chicken manure
TS (% FM)	24.8	33	25	35	40
oTS (% TS)	80	95	89	90	75
Gas yield (m^3t^{-1} FM)	993	270	245	255	225
Methane content (%)	60	52	53	53	55

TS: Total Solid; oTS: organic Total Solid; FM: Fresh Matter.

were determined based on literature (Ertem, 2011; FNR, 2010; KTBL, 2014) (Table 1).

The functional unit (FU) provides a logical basis for comparing the environmental performance of alternatives (ISO, 2006). The main function of these bioenergy systems is the anaerobic digestion of feedstock for biogas production in order to co-generate electricity and heat. Therefore, two FU were chosen: 1 kg of feedstock mixture fed into the digester and 1 MJ of energy production from biogas. The selection of these FUs is in agreement with other biogas LCA studies (Bacenetti et al., 2012; Dressler et al., 2012; Poeschl et al., 2012a).

2.2.2. Feedstock

The total 7227 tons of energy crop were cultivated on 360 ha of agricultural areas yearly: 2190 tons of maize, 657 tons of rye and 4380 tons of grass (based on wet weight). While maize and rye were harvested once a year, grass was harvested three times a year and then ensiled for 6 months. Although it is suggested that ensiling may increase the methane yield and use of correction factors might cause overestimated methane yields (Herrmann et al., 2011; Kreuger et al., 2011; Pakarinen et al., 2011), it is accepted in this study that the changes in wet weight and total solids during ensiling are small and the loss of energy is negligible.

Table 2 provides an overview of the required input for cultivation of energy crops. Emissions from herbicide applications were calculated based on data from Tenuta and Beauchamp (1996), and Lal (2004). Following the ensilage, crops were transported to the biogas plant. Emissions from ensilage were estimated based on data provided by Institut für regenerative Energietechnick Fachhochschule Nordhausen (2013). The transport (12 km) was conducted with a truck consuming 40 L h^{-1} Diesel. The Diesel consumptions of all the vehicles used in the system were provided by the biogas plant owner.

In order to replace the energy crops, 1400 tons of macroalgae with a C to N ratio of 15:1 were collected from German coast of the Baltic Sea. The most common algae types lie on the beaches around the Baltic Sea is filamentous red algae as also determined by Trelleborg municipality (Gradin, 2015). The collected samples consisted of 80% red algae and almost 20% brown algae mixed with some other residues (less than 1%). Algae was harvested from the shore in early September (it starts lying on the beach since April) by The DM Truxor 4700B amphibian with a fork attachment, a collection capacity of 45 m^3h^{-1} and which consumes 12 L Diesel h^{-1}. The vehicle can operate both on land and in water. As proven by WAB Projects, collected samples are almost completely free of sand, although the machine moves quite slowly (Municipality, 2011). The collected algae were transported (150 km) by a 40 ton capacity truck. In order to have a successful anaerobic digestion, the C to N ratio of feedstock mixture should range from 20:1 to 30:1 (Carver et al., 2011; Mata-Alvarez et al., 2000). Macroalgae has typically lower C:N ratio and high S content (1%) and therefore it was important to co-digest with a feedstock high in N and low in S content (0.31%), e.g., chicken manure to achieve adequate values of C:N ratio and sulphur amount. The high sulphate concentration can lead to the formation of H_2S which results in inhibition of methane production; foul odours; sulphur dioxide emissions on combustion of the biogas; and a corrosive environment (Milledge et al., 2014). For that reason, 912.5 tons of annually produced chicken manure (C to N ratio of 30:1 due to its high straw content) were utilized. The feedstock mixture consisted of 40% manure and 60% macroalgae (based on wet weight). The feedstock mixture had a C to N ratio of 21:1 and 0.72% sulphur content (FNR, 2010). The manure was carried by a tractor to the storage (up to 3 months store). The loading capacity of the tractor was 250 kg and the Diesel consumption was 40 L h^{-1}. Nitrogen-based emissions during storage of chicken manure were estimated based on data from Wathes et al. (1997), Nicholson et al. (2004) and Koerkamp (1994). It was assumed that the storage process results in a release of 10% of the ammonium content to the atmosphere.

Table 2
Basic data for the cultivation of the crops.

	Maize	Rye	Grass
Dates			
Sowing	1st of May	1st of October	1st of April
Harvest	20th of September	20th of June	Harvest 1: 1st of April; Harvest 2: 1st of July; Harvest 3: 1st of October
Input (kg ha^{-1})			
Seed	28	110	40
Herbicide	3	3	1
N fertilizer	166	130	38
P_2O_5 fertilizer	72.7	75	70
K_2O fertilizer	180	170	220

Cultivation data of crops are real data of the plant.

2.2.3. Pre-treatment of algae

Macroalgae contain different types of carbohydrates depending on genera. Brown seaweeds lack of easily fermentable sugars. For this reason, it would not be feasible pursuing a standard AD. On the other hand, green and red seaweeds have high levels of easily accessible sugars. Those are represented by floridian starch and xylan in red macroalgae and starch in green macroalgae (Montingelli et al., 2015). The higher amount of red algae therefore could boost the AD process. Therefore, no pretreatments for the breakdown of the carbohydrates were necessary for this study. However, mechanical pre-treatment was applied as described by Alvarado-Morales et al. (2013). The system consists of milling and grinding of harvested macroalgae (particle size 0.5 cm). The energy consumption was estimated to be 38 kWh per ton of dry macroalgae. Moreover, the electrolytic recovery method for heavy metal removal was utilized as described in Stopić et al. (2007). The yearly energy consumption was determined as 61 MW.

Baltic Sea has a salinity of 2 PSU (practical salinity unit and 1 PSU = 1 g L^{-1}) (Matthäus and Ulrich Lass, 1995). Low salt concentrations can stimulate microbial growth, but high salt concentrations ($\geq$10 g L^{-1}) are known to inhibit anaerobic systems through an increase of osmotic pressure or dehydration of methanogenic microorganisms (Barbot et al., 2015). The collection of macroalgae brings along the salinity problem, occasionally. Since the salinity in Baltic Sea is quite low and a possible inhibition of microbial growth through increased salt concentration in the bioreactor was ruled out by Wiese and Konig (2009), in this study the salinity is accepted to create no challenge for the digestion.

2.2.4. Anaerobic digestion

3 digesters with a total volume of 4500 m^3 are operated at the biogas plant. The digesters are temperature-controlled at 42 °C, culture broth is retained for 170 days. A 1% share of total biogas produced at the digesters assumed to leak into the atmosphere. Electricity for the plant operation was supplied from the electrical grid. Biogas was burnt in a 500 kW Combined Heat and Power, which is assumed to run 8552 h per year. 35% of the produced heat was used for temperature control of the digesters and 65% to the chicken housing.

2.2.5. Digestate

Digestate was stored at the plant or near the agricultural field. The storage process resulted in emissions of CH_4, N_2O and NH_3, which vary depending on the seasonal temperature and the nutrient composition of the digestate. The emissions were estimated according to data from De Vries et al. (2012), (Faulstich and Greiff, 2008); Jülich (2008) and Lukehurst et al. (2010).

The digestate provided N, P, and K (De Vries et al., 2012) for the energy crop production. It was transported to the agricultural areas by a truck of a capacity of 40 tons. The quantities of mineral fertilizers that are potentially substituted by the digestate were determined based on the digestate properties and fertilizer exchange values. In addition, the digestate compositions were determined based on the decomposition rates of the feedstock mixture, and organic N available (De Vries et al., 2012; KTBL, 2014).

Digestate is spread by splash plate into arable land. Methods as described by Brentrup et al. (2000) were followed to determine the fertirrigation emissions caused by digestate spreading. Fertirrigation stands for the combined utilization of fertilizers and water. The main difference from normal fertilization is that in this method, fertilizers are added in soluble forms at low amounts but high frequency, which also allows to save large amounts of water (Lucena, 1995). In the system where macroalgae codigested with chicken manure, there were no possibility to have a closed loop, which allows digestate to be used back in the agriculture as fertilizer, because there is no crop production takes place. Therefore, in this system, the digestate is evaluated at the closest agricultural areas in the same region; however its application is extracted from the system boundary.

2.3. Life cycle impact assessment

The function of the life cycle impact assessment step is to pile up the data gathered in the inventory. First, a classification of impact categories is performed, typically replicating a joint mechanism of environmental risk (e.g. global warming and acidification). In the characterization step, the environmental operation listed in the inventory table is translated into points in regard to each impact category (Tukker, 2000). These points deliver an estimation on the relative intensity on an environmental impact category (Goedkoop et al., 2009). To enable the comparison of feedstock, environmental impacts were calculated based on FU.

A combination of impact categories was considered depending on the type of process: global warming (GWP) in kg CO_2-eq, acidification (AP) in kg SO_2-eq, eutrophication (EP) in kg P-eq, and land transformation (LTP) in m^2. GWP is used within the Kyoto Protocol as a metric for weighting the climatic impact of emissions of different GHG's (Shine et al., 2005). Acidification potential accounts for acidification caused by SO_2 and NO_x. Many nitrogen compounds, which are added as fertilizer, acidify soil over the long term because they generate nitrous oxide and nitric acid during the process of nitrification. The production systems were modelled in the Simapro 7.3.2 (PRé Consultants, 2008) by using the Ecoinvent 2.2 database. The effects of emissions in the environment were assessed for a 100-year period, in accordance with the ReCiPe midpoint hierarchist method v.1.06. Midpoint results help to improve the understanding of the complexity of the impacts to emissions to air, water and soil to impact categories. Positive values indicate increased environmental impacts.

3. Results

LCA studies were performed within the system boundaries as shown in Fig. 1. Fig. 2 illustrates the comparison of LCA characterization results (For a detailed overview, see Appendices). When energy production is considered (FU: 1 MJ of energy production), the substitution of energy crops with macroalgae would result in 67%, 95%, 65% and 73% lower GWP, AP, EP and LTP, respectively, due to the avoidance of digestate spreading. When the amount of feedstock for energy production is considered (FU: 1 kg of feedstock fed into the digesters), it can be seen that macroalgae would result in 22% and 15% higher EP and GWP. The different functional units lead to varying results, which underlines the importance of the consideration of relevant FU based on the necessities; either the bioenergy production or the amount of feedstock consumed.

When macroalgae were used, the greatest emission contributor were the digesters (44% of GWP, 32% of AP and 40% of the EP). If the current operation (co-digestion of energy crops with chicken manure) was investigated, it is seen that the digestate spreading contributes the highest to acidification, eutrophication and particulate matter formation potentials due to high nitrate and phosphorous emissions. Crop production creates the highest LTP due to arable land use for bioenergy production, followed by transport. Fuel combustion emissions of the transport cause the highest GWP. The outcomes showed that macroalgae provided highly promising results by means of GHG emissions savings (Fig. 2).

3.1. Greenhouse gas balance

The combustion of biogas (biomethane) is climate neutral, assuming that methane is completely oxidized during biogas combustion. After biomass combustion, carbon dioxide is released back into the atmosphere with no net addition of carbon, as it is consumed during plant growth (photosynthesis) and converted back into biomass. GHG emissions are based on organic carbon depletion in the soil, diesel utilization, nitrous oxide emissions of the plant cultivation process, methane losses during digestion and the process energy input. Gross GHG emissions of the systems are for macroalgae 13.9 g CO_2-eq MJ^{-1} and 160 g CO_2-eq kg^{-1} feedstock, and for energy crops 28.9 g CO_2-eq MJ^{-1} and 140 g CO_2-eq kg^{-1} feedstock, respectively (Fig. 2a).

Naturally, the results of GHG emission savings depend on the type of feedstock. According to Fig. 2a, results suggest that the operation using energy crops has a GWP, which is 52% higher than that in the case of macroalgae. The GWP reductions were caused due to no agricultural activity within the macroalgae scenario. When macroalgae are co-digested with chicken manure, digestion (44%) and digestate storage (38%) contribute the highest to the GWP.

Various LCA studies have analyzed the environmental benefits and the deficiencies of biogas production from different feedstock (Börjesson and Berglund, 2007; Hartmann, 2006). The use of different data, functional units, allocation methods, system

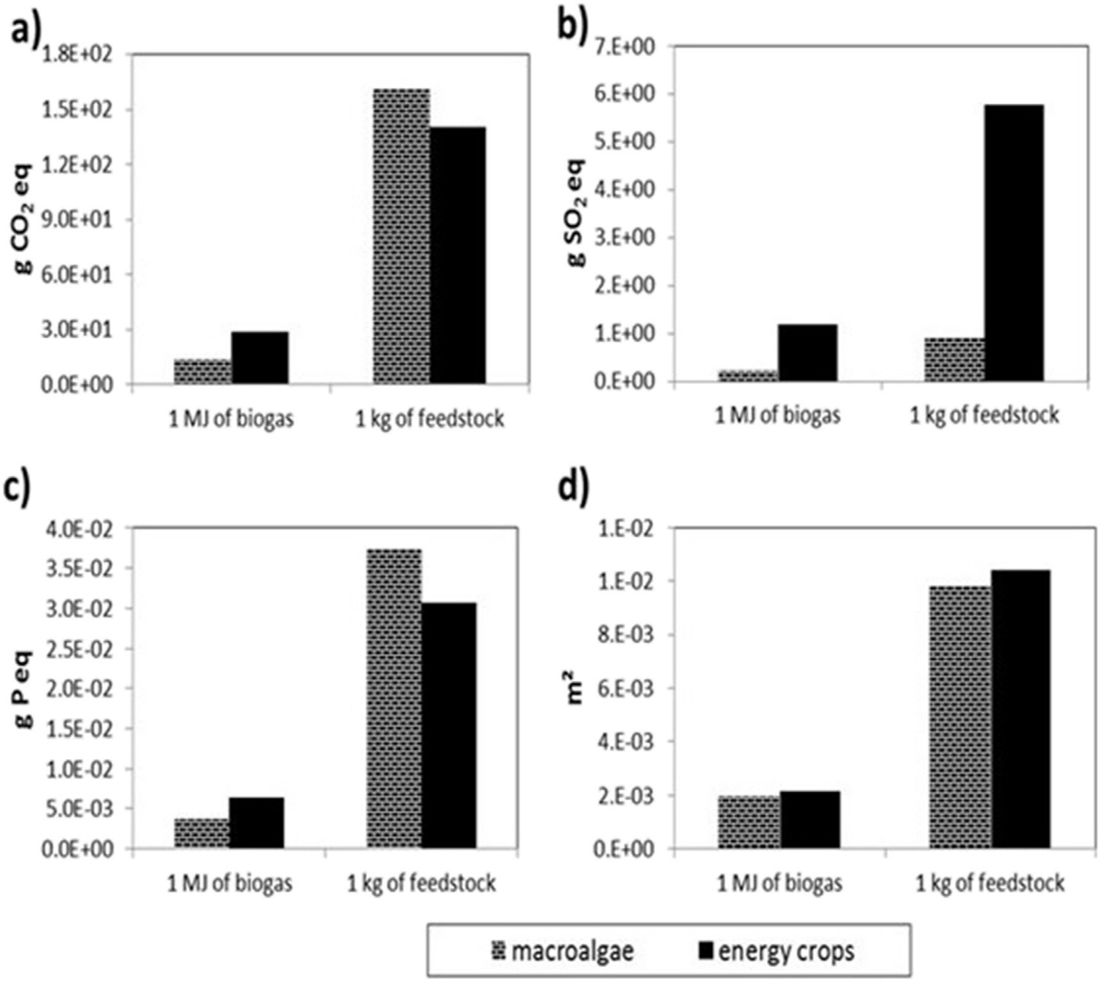

Fig. 2. The comparison of LCA results for energy production with macroalgae and energy crops based on a) global warming, b) acidification, c) eutrophication and d) land transformation. The results are given depending on FU's.

boundaries, impact methods and other assumptions impedes frank comparisons of LCA bioenergy studies (Cherubini and Strømman, 2011). In addition, uncertainties and the use of specific local parameters for indirect effects lead to a wide variability of results (Dressler et al., 2012).

(Poeschl et al., 2012a, b) investigated several digestion scenarios of different feedstock. They derived a GWP of mono-digestion of energy crops at small-scale biogas plants of 113.8, 163.86, 107.62 g CO_2-eq kg^{-1} feedstock for maize, wheat, and grass silage, respectively. They demonstrated that the largest environmental burdens are obtained by the use of energy crops as feedstock due to the higher fossil fuel consumption during the agricultural production.

Bachmaier et al. (2010) investigated the CO_2 emission of 10 biogas plants in Germany that emitted an average of 37.7 g CO_2-eq MJ^{-1}. The authors found out that the electricity production in the biogas plants avoids GHG emissions of 573–910 g CO_2-eq per kWh el. They conclude that a consistent estimate of the GHG emissions of electricity production from biogas can be realized only for individual plants, based on data over a period of at least 1 year. Furthermore, they have concluded that the validity of GHG balances should be improved by supplying reliable data on NO_x emissions from energy crop cultivation, methane leakage from biogas plants and emissions from unsealed digesters. Dressler et al. (2012) investigated the conversion of biogas produced from maize into electricity at several biogas plant within a life cycle assessment view and found out the GWP ranging between 16.1 and 50 g CO_2-eq MJ^{-1}. The authors identified the cultivation of maize as the most influential parameter for the GHG emissions. When the GHG emissions from biogas plants are considered, our study is in agreement with the results provided by other studies.

Not many LCA studies were conducted regarding to the utilization of macroalgae as feedstock for biogas plants. Alvarado-Morales et al. (2013) performed an LCA study for the biogas production from brown macroalgae. The authors showed that the highest GWP originates from macroalgae production. If the production was not considered, the GWP equals to 15 g CO_2-eq MJ^{-1}. In our study macroalgae were not digested alone, but instead co-digested with chicken manure. Low C to N ratio of macroalgae and a high sulphur content could be problematic for anaerobic digestion. Co-digestion with chicken manure (High in N content and low in S) will overcome these problems by increasing the C to N ratio to 21:1 and decreasing the S content to 0.72% (based on the operation of the plant described in this study, see also Section 2.2.2).

3.2. Emissions leading to acidification and eutrophication

Emissions that lead to acidification are on-site an include H_2S, NH_3, SO_2, and NOx emissions. In the current operation, the acidification potential is primarily caused by ammonia and secondly by nitrous oxide release during the application of digestate. Ammonia releases into the atmosphere are mainly caused due to the evaporation and strictly related to the season of the spreading due to differences in temperature. However, the system analyzing the co-digestion of macroalgae and chicken manure does not include any agricultural activities, since all the crop production are excluded from considerations. In this operation style, the highest AP resulted from SO_2 and NO_x emissions created during the collection of macroalgae, followed by Diesel combustion emissions from the transport of algae. This study determined the AP of the current operation system as 5.77. When the energy crops are replaced with macroalgae and co-digested with chicken manure, this potential decreases to 0.89 g SO_2-eq kg^{-1} feedstock (82% lower, Fig. 2b).

The eutrophication balance shows similar trends between the analyzed biogas production systems, as similar findings are reported by other studies (Bühle et al., 2011; Jury et al., 2010). This fact underlines the importance of obtaining feedstock for biogas production under sustainable conditions. Poeschl et al. (2012b) determined the eutrophication potentials of energy crops per kg feedstock as 0.01, 0.03, 0.09 g P-eq for maize, grass, wheat silage, respectively. This study determined the EP of the current operation style as 0.03 g P-eq kg^{-1} feedstock and the EP of the co-digestion of macroalgae and chicken manure as 0.037 g P-eq kg^{-1} feedstock (Fig. 2c).

For the current operation, the EP mainly depends on the phosphate content of digestate (applied P per ha during spreading) and the emissions from the main digester. Emissions of the main digester create the highest EP, when macroalgae are used. These emissions could have been avoided, if ammonia filters were applied (Deublein and Steinhauser, 2011).

3.3. Natural land transformation

When the FU per kg feedstock is considered, LTP was determined as 0.01 m^2 for energy crops and 0.0098 m^2 for macroalgae. LTP (Fig 2d) were mainly related to transport and agricultural crop production. When energy crops are substituted with macroalgae, the LTP is reduced by 2%, which is due to the unnecessity of agricultural production. If the biogas plant was located in a 50 km distance to the coastline, the LTP would be 0.009 m^2, at a distance of 150 km, it rises by 12%. Thus, the transport distance has a huge impact on the LTP.

4. Discussions

4.1. Limitations of the study

Although no sensitivity analysis was performed in this study, the chosen factors were based on practical considerations and thus are relevant as they can be substituted or changed in a real case. However, all chosen values, e.g. to model harvest, depend on many factors as the type of vehicle, fuel consumption, its capacity, etc., which cannot be varied for every plausible case. Analyzing the impacts of regional factors would be topic of further research, since this study has a limited scope. Another limitation lies in the restricted consideration of all possible pretreatment methods for macroalgae. However, as aforementioned pretreatment methods to be applied mainly depends on the vehicle chosen, The vehicle chosen in this study makes it sure that there is no sand accumulation in the harvested biomass. Only disadvantage of the vehicle is its long working hour requirements, since it moves quite slowly. Regarding any other inorganics or heavy metals, our study has already investigated the mechanical and electrolytic pretreatment. As described before, salinity could have been a problem, if the algae would have harvested from different regions or from another coastal line of another Sea except of Baltic Sea. This also requires further research regarding to impacts of region on the harvested biomass properties.

4.2. Limitations and benefits of biogas production with algal feedstock

Biogas is currently produced mainly from land-based crops. A constant utilization of these crops leads to a food versus energy argumentation. A feedstock is required, which is plentiful and carbohydrate-rich. The production of such a crop should not require the utilization of pesticides, herbicides, and a vast amount of fertilizer. Marine biomass could encounter these challenges, since it is an abundant, carbon neutral renewable resource with potential to diminish GHG emissions and the climate change impact.

However, a low interest in algal biomass as an alternative source of biodegradable organic matter applied in biogas production systems is mainly due to technological and technical difficulties in process operation due to a complex harvest of macroalgal biomass acquisition, high initial hydration of biomass, difficulties with its storage and high costs of its dehydration. Other main technology-related issues include the selection of an appropriate retention time, and methods of biomass conditioning and pretreatment (González-Fernández et al., 2011; Wu et al., 2010; Yuan et al., 2011). If the pretreatment is not conducted appropriately, macroalgae reduce or completely inhibit biogas formation (Bruhn et al., 2011; Chynoweth et al., 1993; Guo, 2007; Ras et al., 2011; Yen and Brune, 2007; Zeng et al., 2010). If the high protein content is not considered, it may lead to enhanced production of free ammonia and volatile fatty acids. They elicit toxic effects on methanogenesis. In addition, sodium ions in the algal biomass may inhibit the biogas production as well (Dębowski et al., 2013). The high sulphate concentration which is typical for green macroalgae can also lead to inhibition in the fermentation process as proven by Hilton and Archer (1988); Murphy et al. (2013).

In comparison to biomass crops, macroalgae comprise little cellulose, no lignin and a low C:N ratio (Wu et al., 2010). However, the C to N ratio of feedstock should range from 20:1 to 30:1 (Carver et al., 2011; Mata-Alvarez et al., 2000). The most accurate evaluation of the industrial potential of methane production from macroalgae was performed by Matsui et al. (2006) using a commercial scale 4-stage anaerobic digester, with a daily input between 0.2 and 1.0 tons of macroalgae at a retention time of 15–25 days. This resulted in an average production of 22 m^3 of methane per ton wet weight of brown macroalgae. However, recent advances suggest there is still potential for further optimizing biogas yields through co-digestion with a more nitrogenous substrate, for example chicken manure or maize silage. Mussgnug et al. (2010) tested the co-digestion of macroalgae with maize silage and concluded that this operation results in a higher yield of methane fermentation under the same technological conditions. Ertem (2011) demonstrated that under same mesophilic conditions with 10% inoculum addition, mono digestion of macro algae would result in lower biogas yields, compared to energy crops; 84.5 m^3t^{-1}VS for the mixture of brown&red algae, 578.9 m^3t^{-1}VS for sugar beet 107.9 m^3t^{-1}VS for straw, 461.6 m^3t^{-1}VS for maize.

Despite some limitations of algal biomass utilization for biogas production processes, the studies conducted so far enable acknowledging it as an alternative and prospective source of organic substrate. Macroalgae have many advantages over typical, higher energetic crops. The algae, especially the marine macroalgae contains high quantities of polysaccharides and lipid and arefree of sparingly-degradable lignocellulose compounds (Vergara-Fernández et al., 2008). The biomass of algae serves as a source of nitrogen and important microelements (cobalt, iron, nickel) for the appropriate growth of anaerobic microorganisms (Mata-Alvarez et al., 2000). Macroalgae grow by a higher rate than energy crops, whilst the feasibility of harvesting can make them a competitor on the feedstock market (Rittmann, 2008): According to Gao and McKinley (1994) uncultivated growth of brown and red algae is equivalent to 165–565 t ha^{-1} fresh weight per year, while this growth according to our values equals to 35, 6 and 67 t ha^{-1} fresh weight per year for maize, rye and grass, respectively.

5. Conclusions

The principal aim of this study was to assess the environmental load of macroalgae-based feedstock for the operation of a biogas process throughout the whole life cycle. Our results determine the affirmative impact of algae on the emission reductions: 52%, 83%, 41% and 8% lower global warming, acidification, eutrophication and land transformation potentials, respectively for 1 MJ of biogas production, moreover, 84% and 6% lower acidification and land transformation potentials for 1 ton of feedstock. However, based on the consideration aspect, the results could be debatable. Here one should answer a simple question: what should be considered as resulting in the lowest environmental damage: is it producing the highest possible amount of energy or using the lowest amount of feedstock?

When the aim is producing higher amounts of energy, substituting energy crops with macroalgal biomass is liable, because it helps to solve the dilemma between bioenergy and food production. On the other hand, when the amount of feedstock to be transported and fed into the digesters are the concern, it would be beneficial to analyze the whole system based on the FU of 1 kg feedstock: In this case, the energy crops could be more favorable to mitigate the negative environmental effects of biogas plants.

The outcomes indicate that sustainable energy production is achievable with the co-digestion of chicken manure (40%) and macroalgae (60%). The collection of the algal biomass from the costal lines for biogas production purposes would considerably reduce the total farmland effects caused by terrestrial crop production.

However, in order to produce bioenergy in the form of methane from macroalgae, it will be necessary to:

- Optimize the pre-treatment to improve the performance of a substrate for AD and to ensure that the digestate from the biogas production can be returned to the farmers and re-used as fertilizer.
- Overcome toxicity caused by high levels of phenols, heavy metals, sulfides, salts, and volatile acid compounds found in seaweeds, which can inhibit methanogenesis.
- Optimize harvesting procedures to minimize environmental impacts and overall costs.

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Abbreviations

AP	acidification potential
GWP	global warming potential
GHG	greenhouse gas
EP	eutrophication potential
FU	functional unit
LCA	life cycle assessment
LTP	land transformation potential
oTS	organic total solid
RE	renewable energy
TS	total solid

Appendices

Table A1
LCA characterization results inventory for energy crops based on two functional units: 1 MJ of biogas (FU1), 1 ton of feedstock (FU2).

Process units	GWP (kg CO_2eq)		AP (kg SO_2eq)		EP (kg Peq)		LTP (m^2)	
	FU1	FU2	FU1	FU2	FU1	FU2	FU1	FU2
Crop production[a]	2.64	1.28E+01	1.59E-02	7.72E-02	7.75E-04	3.76E-03	1.35E-03	6.56E-03
Storage[b]	9.96E-01	4.83	1.06E-02	5.14E-02	1.38E-04	6.68E-04	2.85E-05	1.38E-04
Transport[c]	1.30E+01	6.32E+01	9.20E-02	4.46E-01	4.07E-04	1.97E-03	6.26E-04	3.04E-03
Others[d]	1.22E+01	5.93E+01	1.07	5.20	5.02	2.43E-02	1.38E-04	6.71E-04

[a] Maize, rye and grass production.
[b] Storage of crops, manure and digestate.
[c] Transport of crops, manure and digestate.
[d] Fermentation, heat and electricity production from biogas and digestate spreading.

Table A2
LCA characterization results inventory for macroalgae based on two functional units: 1 MJ of biogas (FU1), 1 ton of feedstock (FU2).

Process units	GWP (kg CO_2eq)		AP (kg SO_2eq)		EP (kg Peq)		LTP (m^2)	
	FU1	FU2	FU1	FU2	FU1	FU2	FU1	FU2
Algae harvest[a]	2.10E+00	2.43E+01	7.62E-02	3.31E-01	1.15E-03	1.16E-02	6.11E-04	3.05E-03
Pretreatment[b]	1.32E+00	1.53E+01	1.27E-02	5.51E-02	6.95E-05	7.04E-04	2.03E-04	1.01E-03
Storage[c]	5.50E-01	6.37E+00	6.41E-03	2.79E-02	6.93E-05	7.03E-04	1.02E-05	5.08E-05
Transport[d]	7.77E+00	8.99E+01	1.08E-01	4.68E-01	6.63E-04	6.72E-03	1.00E-03	5.02E-03
Others[e]	2.16E+00	2.50E+01	3.03E-03	1.32E-02	1.75E-03	1.78E-02	1.38E-04	6.92E-04

[a] Harvesting of macroalgae from coastal line.
[b] Mechanical and electrolytic pretreatment of macroalgae.
[c] Transport of macroalgal biomass, manure and digestate.
[d] Transport of macroalgae, manure and digestate.
[e] Fermentation, heat and electricity production from biogas.

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