Sebastian Foth, Jan Sprafke, Michael Nelles

COASTAL Biogas – Utilization of seaweed (*Zostera marina*) as co-substrate in anaerobic digestion

Abstract: *In Mecklenburg-Western Pomerania, more than 300 km of beaches used for tourism are cleaned of washed-up seaweed. This is mainly done for aesthetic reasons in the main tourist season between April and October (Aldag 2018). Due to harvesting, transport, storage and disposal, beach cleaning represents a large investment for municipalities. Therefore, energy recovery offers the opportunity to refinance costs incurred for beach cleaning. In addition, use of the digestate as fertilizer in agriculture is a valuable addition to efforts to reduce eutrophication in the Baltic Sea. To demonstrate the suitability of seaweed as a co-substrate in anaerobic digestion, using Zostera marina as an example, a 28-day CSTR (continuous-stirred tank reactor) semi-continuous digestion trial was conducted. The specific biogas yields were determined in comparison to corn silage. In addition, it was investigated whether there are differences between fresh and stored seaweed. The results show that seaweed is suitable for the utilization in anaerobic digestion in accordance with legal requirements. There are also differences with regard to the quality of the substrate used.*

Zusammenfassung: *In Mecklenburg-Vorpommern werden über 300 km touristisch genutzter Strände von angespültem Seegras gereinigt. Dies geschieht überwiegend aus Gründen der Ästhetik in der Hauptreisezeit zwischen April und Oktober (Aldag 2018). Durch Ernte, Transport, Lagerung und Entsorgung stellt die Strandreinigung eine große Investition für Kommunen dar. Die energetische Verwertung bietet daher die Möglichkeit anfallende Kosten für die Strandreinigung zu refinanzieren. Zudem ist die Nutzung der Gärrückstände als Dünger in der Landwirtschaft eine wertvolle Ergänzung zu den Bemühungen zur Minderung der Eutrophierung in der Ostsee. Um die Eignung von Seegras als Co-Substrat in der anaeroben Vergärung, am Beispiel von Zostera marina, nachzuweisen, wurde ein 28-tägiger CSTR-semikontinuierlicher Gärversuch durchgeführt. Es wurden die spezifischen Biogaserträge im Vergleich zu Mais-Silage ermittelt. Darüber hinaus wurde untersucht, ob es Unterschiede zwischen frischem und gelagertem Seegras gibt. Die Ergebnisse zeigen, dass Seegras zur energetischen Verwertung als Co-Substrat in der anaeroben Vergärung gemäß gesetzlichen Grundlagen geeignet ist. Es ergeben sich zudem Unterschiede im Hinblick auf die Qualität des eingesetzten Substrates.*

Introduction

According to Boström et al. (2014), approximately 155 km² of the German Baltic Sea coast are colonized by seaweed meadows. They are providing a lot of services fort the ecosystem. Their roots serve as natural erosion protection for the sediment. They have a high importance as a food and breeding habitat and can absorb excess nutrients (Schubert et al. 2015). The seaweed meadows of the German Baltic Sea coast are populated mainly by Zostera marina (Boström et al. 2014). At the end of a vegetation period, dead and torn-off plant components flushed to the coasts by wind and flow-induced hydrodynamic processes (Grave & Möller 1982). The amount of seaweed washed on shore depends highly on location and exposure of the beaches as well as acute weather events (Ptacnikova 2013). In Mecklenburg-Western Pomerania, an estimated 17,500 tons land on touristic beaches each year (State parliament of Mecklenburg-Western Pomerania 2017, Ministerium für Wirtschaft, Arbeit und Tourismus 2019). Traditionally, intensively used bathing beaches are cleaned of beach wrack, as the majority of bathing tourists and inhabitants prefer a clean and white beach. Municipalities spend big financial efforts for harvesting, transport, storage and disposing the material.

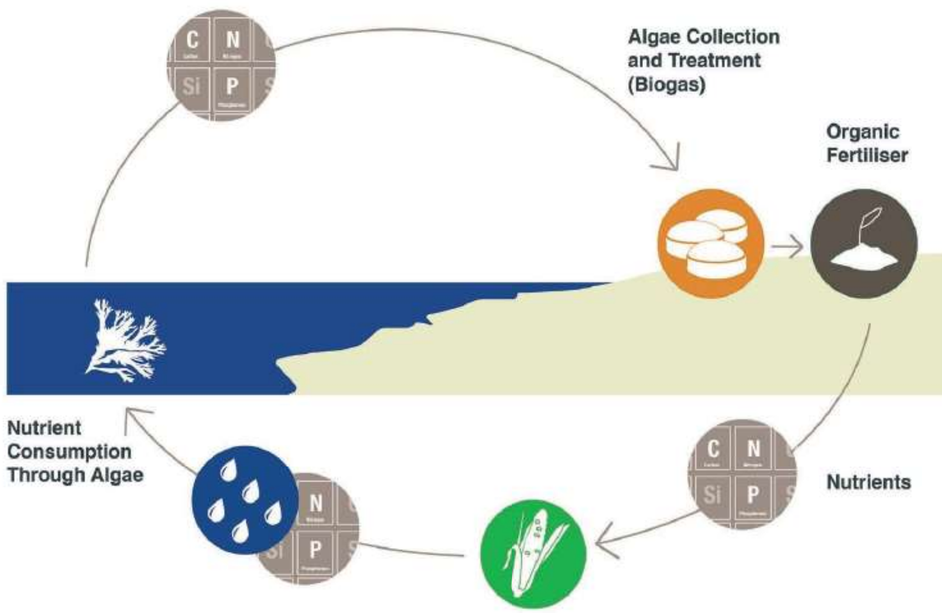

Fig. 1: Closed nutrient cycle by using seaweed Source: COASTAL Biogas

Within the project "COASTAL Biogas" (STHB.02.02.00-DE-0129/17) the Department of Waste and Resource Management in Rostock investigates the possibilities for commercial utilization of washed-up seaweed at the Baltic Sea coast. The focus of this research is the energetic utilization as co-substrate in anaerobic digestion. The resulting digestates are used as fertilizer on agricultural land. By establishing this value chain from washed-up seaweed, this project aims to combat eutrophication in the Baltic Sea and relieve the financial burden on beach cleaning (Fig. 1). In the past few years, the commercial utilization of seaweed has become an increasingly important economically and ecologically issue. In addition to the decentralized occurrence and the discontinuous availability of the material, the properties of the substrate are the most important criterion for utilization. These can differ widely in space and time. The objective of the study was to prove the suitability of seaweed as a co-substrate in anaerobic digestion. Using *Zostera marina* as example, various analyses of the substrate were made as well as a 28-day CSTR trial in lab scale. Additionally, the possible influence of storage time on substrate quality was investigated.

Study area and sampling

We did a single sampling on 09.03.2020 after a storm event in Klein Strömkendorf, a beach section on the Baltic Sea coast of Mecklenburg-Western Pomerania (Fig. 2). Klein Strömkendorf is located in the west of the state near Pepelow, a popular destination for tourists and locals. The selected beach section is a bit aside from the tourist beaches. In this coastal section, beach and shore are narrow but strongly structured partly by stones. There is also a cliff. The terrain changes constantly by flood events to a more or less extent.

Fig. 2: Study area: Beach of Klein Strömkendorf

Approximately 100 kg fresh matter of seaweed was collected. The sample consisted completely of Zostera marina (Fig. 3). We washed the sample and cleaned it of impurities (sand, shells, etc.). The sample was divided int two batches. One sample was fresh frozen. The second sample was stored for 60 days under realistic conditions. The storage unit was not covered but drained. Leachate/rainwater could run off but was not collected separately. In addition to seaweed, corn silage was obtained as a comparative substrate from a nearby biogas plant for the experiments.

Fig. 3: Fresh substrate (on the beach and washed): Zostera marina

Subsequently, the substrates were subjected to an input analysis in the course of the trial preparation. Total solids (TS) and volatile solids (VS) were determined as well as as well as XF, ADF and NDF.

Tab. 1: Results input analysis

Substrate	TS	VS	XF	ADF	NDF
Unit	%	%	% VS	% VS	% VS
Corn Silage	30.8	29.7	-	-	-
Zostera marina (fresh)	10.6	8.4	35.1	32.8	41.5
Zostera marina (stored)	74.9	55.6	30.4	30.6	36.9

Methodology

The study investigates the energetic utilization of seaweed (Zostera marina) from beach cleaning measures as Co-substrate in anaerobic digestion. The investigations were carried out in the laboratory of the Department of Waste and Resource Management at the University of Rostock. The main focus lies on the examination of the specific biogas yield of seaweed concerning the energy recovery in co-digestion with corn silage as well as the suitability of digestates as fertilizer in agriculture.

Semi-continuous fermentation experiment

A CSTR with a total volume of 20 L and a working volume of 10 L was used for the semi-continuous fermentation experiment (Fig. 4). The individual fermenters are equipped with a variable speed agitator with adjustable intervals. The motor of the stirrer was placed below the reactor. The process temperature was adjusted to 38 °C using a heater and a thermostat. The reactor has a feeding tube extending from the top to below the filling level. The biogas quantity is measured and continuously recorded with drum gas meters. Biogas production, temperature and air pressure were recorded by a data logger.

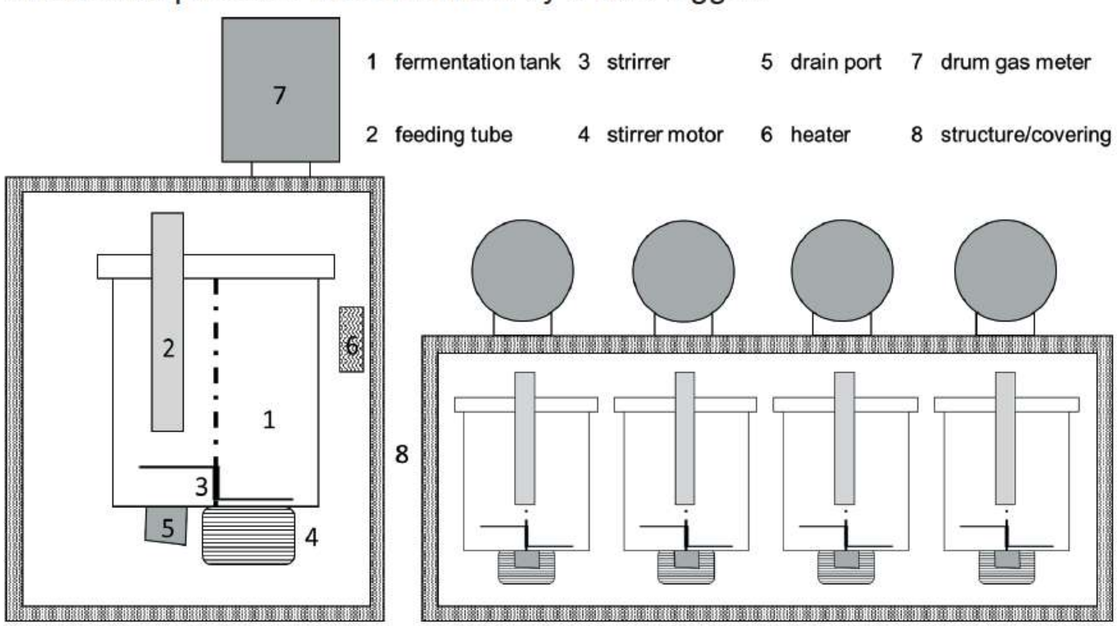

Fig. 4: Schematic of a used tank reactor from the side and front

In addition to seaweed, corn silage was also investigated as a comparative substrate in mono-digestion. In addition, both substrates were investigated together in different mixing ratios in co-digestion. The inoculum used was digested sludge from the wastewater treatment plant in Rostock with a TS content of 2.9 % and an VS content of 1.4 %. Three fermenter groups were operated for 28 days. One group was operated for mono-digestion of corn silage over 28 days. The second group was operated with 90 % corn silage and 10 % fresh seaweed. The third group was operated with 90 % corn silage and 10 % stored seaweed. An organic loading rate (OLR) of 2.02 kgVS/(m^3*d) was adjusted for the experimental setup. The amounts for feeding were calculated and prepared accordingly. The substrate was supplied to the fermenters once a day, 5 days a week. An adjusted, distributed feeding was chosen according to the recommendation in Lincke and Schwarz (2013), where Monday is given 160 %, Tuesday and Wednesday each 80 %, and Thursday and Friday each 90 % of the mean feeding amount of 20 g VS per day. The weekly feeding was consequently 100 g VS. This amount was kept for the entire duration of the experiment.

Tab. 2: Experimental set-up

	Group 1	**Group 2**	**Group 3**
Substrate	100 % corn silage	10 % fresh seaweed	10 % stored seaweed
Duration	28 days	28 days	28 days
FM/week	336.50 g	362.20g	310 g

Samples of digestate were taken once a week via the feeding tube at the top of the reactor. Samples of digestates were analyzed directly after sampling. TS and VS were measured in the original samples (as mixed sample for the whole group) without pre-treatment. Additionally, one sample of each reactor sample was centrifuged for 30 min at 20.000 rpm. Volatile Organic Acids Content (FOS) and Buffer Capacity (TAC) were determined (titration) for each individual fermenter. Three times a week samples of biogas were taken, and its biogas composition (methane, CO_2, and O_2 percentages) was determined with a multi-gas measuring device of the type Visit 03 (Messtechnik Eheim GmbH). A gas sample from a reactor was used as the calibration gas before. The evaluation was carried out on a weekly basis. For this purpose, all measurement data from Monday 0:00 to Sunday 23:59 were combined into a measurement block and evaluated.

Results

Table 3 summarizes the cumulative biogas and methane yield over the entire duration of the experiment. Group 1 and group 2 show the highest values.

Tab 3: Cumulative biogas and methane yields in l(n)/kg VS

	Group 1	Group 2	Group 3
Substrate	100 % corn silage	10 % fresh seaweed	10 % stored seaweed
Biogas	262.3	253.2	237.1
Methan	129.5	125.5	114.1

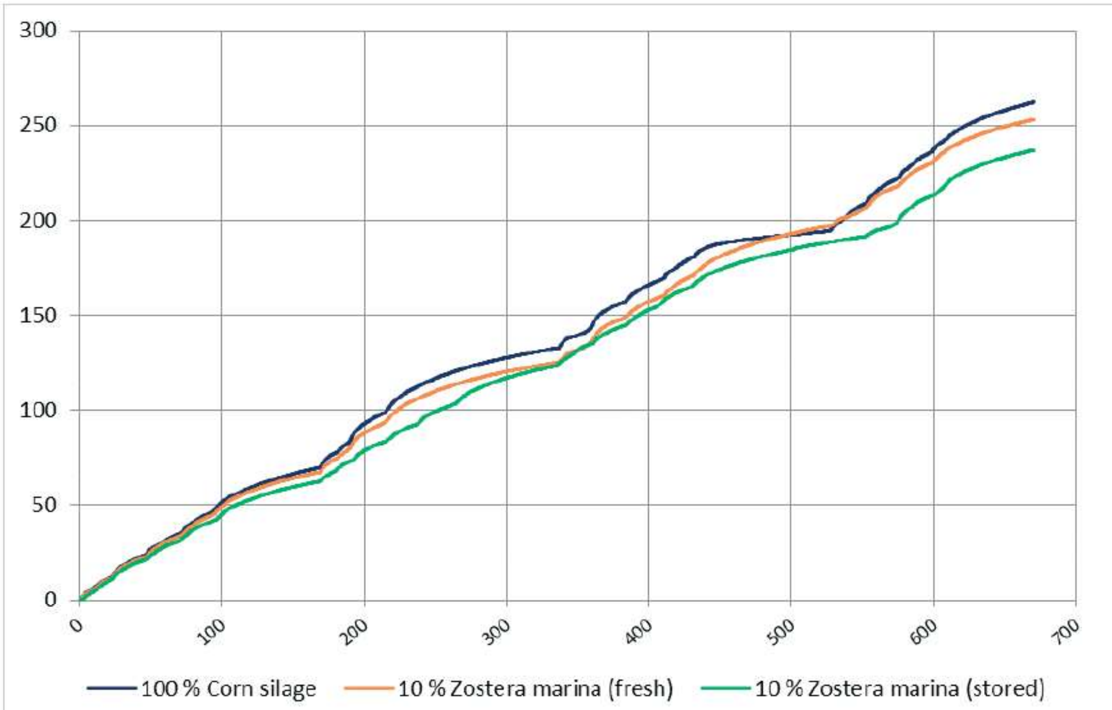

Fig 5: Cumulative biogas volume of corn silage and mixtures with Zostera marina

The cumulative biogas volume presented in Fig. 5 shows an overall very similar trend in all three groups. Nevertheless, the gas yield of group 1 is constantly the highest. Group 2 rarely differs from the values recorded. Only group 3 shows a visibly lower biogas yield over the trial period. This trend is also consistent in the determined values for the specific biogas and methane yields (Tab. 5). Group on with 100 % corn silage has the highest biogas and methane yield. The mixture with 10 % fresh matter of Zostera marina hardly differs from it. Group 3 with 10 % stored matter of Zostera marina has the lowest yields of biogas and methane.

Tab 4: Specific biogas and methane yield of corn silage and mixtures with Zostera marina in l(n)/g VS

	Group 1	Group 2	Group 3
Substrate	100 % corn silage	10 % fresh seaweed	10 % stored seaweed
Biogas	0.656	0.633	0.593
Methan	0.324	0.314	0.285

In relation to used dry matter from stored Zostera marina, a specific biogas yield of 0.290 l(n)/g VS and a methane yield of 0.139 l(n)/g VS were calculated, which would comply to the use of the substrate in mono-digestion. For fresh Zostera marina, no corresponding value could be determined with the applied calculation approach, because the VS used in the mixture was too low. The average methane content was 49.4 % in group 1, 49.5 % in group 2 and 48,1 % in group 3. In order to be able, evaluate the collected data according to the specific methane yield, the following table shows comparative values of selected aquatic substrates in anaerobic digestion from the literature.

Tab. 5: Comparative values of selected substrates in anaerobic digestion

Substrate	**Methane Yield**
unit	m^3/t VS
Seaweed (unspecific)[1]	211
***Zostera marina*[2]**	100
Macroalgae (February)[3]	125
Macroalgae (April/May)[3]	200
***Fucus vesiculosus*[3]**	442
***Palmaria palmata*[3]**	453
Corn silage[4]	370

[1] *Fredenslund et al. (2011)*
[2] *Tyge Kjaer (2019)*
[3] *COASTAL Biogas Report 3.3 (2020)*
[4] *Deutscher Verband für Landschaftspflege e.V. (2014)*

The following table summarizes the results of the digestate analysis. The FOS/TAC values are overall within the standard conditions. Moreover, there are no noticeable differences. The collected data on TS, VS appear uniform and not with increased dry matter in relation to the initial inoculum.

Tab. 6: Results of the digestate analysis

	Group	**FOS/TAC**	**pH**
I	100 % corn silage	0.194	7.83
II	10 % fresh seaweed	0.197	7.88
III	10 % stored seaweed	0.201	7.89

Value creation from seaweed through energy use in biogas plants also includes the utilization of the digestate. The elemental composition is essential for this, especially with regard to macronutrients and heavy metals. For the digestate from group 1 and group 2 as well as the original substrates corn silage and fresh Zostera marina, the following tables 7 and 8 show the contents of C, N, P and the heavy metals Cd, Mn and Pb.

Tab. 7: Contents of Macronutrients C, N, P

	C	N	P
Unit	% VS	g/kg VS	g/kg VS
Digestate 100 % Corn silage	36.2	28.4	10.8
Digestate 10 % Zostera marina (fresh)	36.1	28.8	9.4
OS Zostera marina (fresh)	35.5	17.1	1.2
OS Corn silage	43.9	14.3	2.5

Tab.8: Contents of heavy metals Cd, Mn, Pb

	Cd	Mn	Pb
Unit	mg/kg VS	mg/kg VS	mg/kg VS
Digestate 100 % Corn silage	0.22	250	0.89
Digestate 10 % Zostera marina (fresh)	0.24	229	1.08
OS Zostera marina (fresh)	0.51	254	1.90
OS Corn silage	0.03	20	0.17

Discussion

The material use of seaweeds has a long history in the Baltic Sea region, both as a building material and as a fertilizer (Aldag 2018). The energetic use of seaweed as a co-substrate in biogas plants is becoming increasingly important, especially in Scandinavia. In comparison to conventional energy crops, water plants are not standing in a competition to animal feed or food. In addition to quantity and quality as well as the economic efficiency of the management concepts the utilization depends also on political hurdles (Buschmann et al. 2017). Washed up seaweed is declared in the European Waste List under waste code number 20 02 01 (biodegradable waste) and is considered as vegetable waste from a source other than households. It belongs therefore to the municipal waste and has to be disposed/recycled under consideration of waste law aspects. The field of waste law application is opened at the moment when the biomass is collected after beach cleaning for further management (Landtag Mecklenburg-Vorpommern 2017). If the biomass and its products is used as a fertilizer the limit values for nutrients heavy metals must be complied. A verification procedure must be carried out for this purpose. In addition, the provisions of the Fertilizer Ordinance (DüMV) and the Fertilizer Ordinance (DüV) must be taken into account (Aldag 2018).

The amount and composition of washed up seagrass varies spatially and temporally. In this study, *Zostera marina* is evaluated as a representative of the seaweed resources in the Baltic Sea with regard to its suitability for fermentation as a co-substrate in biogas plants. Pure occurrences of *Zostera marina* are possible after certain weather events (Boström et al. 2014). Furthermore, the quality of the biomass strongly depends on the age of the plant fragments and the residence time on the beach as well as pre-treatment. In this study, freshly harvested and stored substrate were considered in 10% mixtures with corn silage. In relation to the annual theoretical potential of seaweed in Mecklenburg-Western Pomerania (Foth et al. 2020), this proportion seems realistic.

The results of the biogas trials in place well in the selection of comparative values from the literature in terms of the determined cumulative volumes used substrates in mono-digestion as well as in co-digestion. Overall, the yields obtained from the mixtures rarely differed from those of the control group with 100% corn silage. Nevertheless, higher yields seem to be generated from the fresh substrate than from the stored substrate. Also, the measured methane contents are lower when using stored substrate compared to corn silage and the mixture with 10% fresh seaweed. In this context, Prof. Dr. Jens Born from the Competence Center Biomass Utilization of the Flensburg University of Applied Sciences explains in his presentation about disposal and utilization options of beach wrack the influence of storage on specific biogas yields. Storage losses due to decomposition processes as well as emission of potent leachate and washing out of the substrate by precipitation have a negative effect. Therefore, to increase yields from stored seaweed, covered storage of biomass in tunnels in combination with collection of the leachate and subsequent fermentation in the biogas process (Born 2014) is recomment. Since in this study the storage took place without roofing and the collection of leachate unfortunately, no concrete statements can be made in this regard. However, the experimental results show both, the variation of differently treated substrates and respectively the suitability of Zostera marina as Co-Substrate in anaerobic digestion. The Results of the input analysis show anyway, that stored material has lower percentages of XF, ADF und NDF. The VS content is also much higher. This is related to ensiling processes during storage, which increases digestibility and biogas yield of fiber-containing and lignocellulosic substrates (Gallegos et al. 2018). ADF for example is a measure of the plant components in forages that are the least digestible by livestock, including cellulose and lignin. According to feed analysis, high values mean poorer conversion. Since fresh seaweed has a higher proportion of ADF, it seems to be generally more difficult to decompose.

The elemental analysis shows no critical loads with concern to the initial substrate. However, the elemental composition can vary strongly not only in time (COASTAL Biogas Report 3.2) but also in space. This is shown by collected data from spring 2020. We made a one site sampling from 13 different locations along the Baltic Sea Coast of Mecklenburg-Western Pomerania (Fig. 6), 7 in April, 6 in May, after Storm events. We concentrate our sampling also on the species *Zostera marina*. The focus of investigation was on important elements for plant growing like macronutrient and alkali metals as well as impurities like heavy metals. Most of the lab test were made in external laboratories.

Fig. 6: Investigation area of elemental analysis

Tab. 9: Contents of the macronutrients C, N, P and the heavy metals Cd, Mn and Pb

	C	N	P	Cd	Mn	Pb
Unit	% VS	g/kg VS	g/kg VS	mg/kg VS	mg/kg VS	mg/kg VS
1	33.4	23.8	1.9	0.73	111	0.8
2	35.5	17.1	1.2	0.51	253	1.9
3	39.9	31.5	4	0.68	685	1.9
4	38.7	24.3	1.9	1.6	240	1.5
5	39.6	22.4	1.5	1.7	498	1.3
6	32.7	20.3	1.5	1.2	247	5.1
7	34.1	20.9	1.1	0.6	246	2.6
8	37.1	23.7	2.5	1.5	210	1.2
9	31.5	20.7	1.4	1.9	254	2.2
10	35.1	21.3	1.9	2	409	3.79
11	38	21.1	2.8	1.1	211	0.7
12	37.7	22.6	2.3	1.3	473	3.18
13	34	23.6	2.4	1.4	340	1.7
Grenzwerte[1]	-	-	-	1.5	200	150
[1] Düngemittelverordnung (DüMV)						

Some samples are over the limit values of Cadmium and Manganese but not in general. And the results from the digestate analysis show that the addition of 10 % *Zostera marina* to the digested mixture has no significant negative effect on the elemental composition of the digestate in terms of limit values for nutrients and heavy metals. The digestate produced in this experiment is suitable for utilization on agricultural land.

Conclusion

This study proves the suitability of *Zostera marina* as a co-substrate in biogas plants as well as the suitability of the digestate on agricultural land. Consequently, this study follows the assessments of the literature (Ministry of Economy, Labor and Tourism 2009). The yields depend on the seasonal differentiation of the substrate in quantity and composition as well as the treatment of the substrate (Born 2014). In order to make more precise statements on spatial and temporal variations in species composition, substance accumulation, etc. concerning to the utilization potential further studies are necessary.

The technical literature as well as authorities provide recommendations for pretreatment, utilization as well as legal frameworks (Ministry of Economy, Labor and Health 2018). However, transportation and disposal are a financial burden on municipalities. And since the potential profit from anaerobic digestion do not flow back into the expenses for beach cleaning, it is a difficult substrate for the disposer. In addition, there is too little networking among stakeholders and too few specific support programs from decision makers with concrete solution strategies. Consequently, with the exception of a few committed municipalities that are willing to work together with other partners on the recycling of seaweed, no area-wide value creation takes place. Seaweed processing must fit into a sensible disposal concept by considering anaerobic digestion as a process to reduce biological load and reduce disposal costs (Born 2014). If the washed-up seaweed is not collected and recycled, the contained nutrients are released back to the Baltic sea (Lybaek 2014). The establishment of a value chain provides therefore a valuable addition to the reduction of eutrophication in the Baltic Sea and for the circular bioeconomy in Mecklenburg-Western Pomerania.

References

Aldag, S. (2018): Ökologische Aspekte der stofflichen Verwertung von Seegras, Rostock

Born, J. (2014): Treibselentsorgung und –verwertungsmöglichkeiten, Referat

Boström et al. (2014): Distribution, structure and function of Nordic eelgrass (Zostera marina) ecosystems: implications for coastal management and conservation

Buschmann et al. (2017): Seaweed production: overview of the global state of exploitation, farming and emerging research activity

COASTAL Biogas Report 3.2 (2020): A report on operating biogas facilities utilising anaerobic digestion of cast seaweed

COASTAL Biogas Report 3.3 (2020): Report on potential of cast seaweed and policy frameworks in South Baltic Sea area

Deutscher Verband für Landschaftspflege e.V. (2014): Vom Landschaftspflegematerial zum Biogas – ein Beratungsordner

DüMV (2012): Verordnung über das Inverkehrbringen von Düngemitteln, Bodenhilfsstoffen, Kultursubstraten und Pflanzenhilfsmitteln (Düngemittelverordnung - DüMV)

Fredenslund, A. M., Christensen, T. B., Kjær, T., Danielsen, S., Møller, H. B., Kjær, L. L., & Fafner, K. (2011): Utilization of cast seaweed and waste from pectin production for anaerobic digestion. In Proceedings Sardinia 2011, Thirteenth International Waste Management and Landfill Symposium Sardinia 2011 Proceedings – Thirteenth International Waste Management and Landfill Symposium

Foth, S., Schüch, A., Nelles, M. (2020) : COASTAL Biogas – Energetische Verwertung von Seegras als Co-Substrat in der anaeroben Vergärung

Gallegos, D., Wedwitschka, H., Moeller, L., Weinrich, S., Zehnsdorf, A., Nelles, M., Stinner, W. (2018): Mixed silage of Elodea and wheat straw as a substrate for energy production in anaerobic digestion plants, Energy, Sustainability and Society

GRAVE, H., MÖLLER, H. (1982): Quantifizierung des pflanzlichen Strandanwurfs an der westdeutschen Ostseeküste

Kjaer, Tyge (2019): Experiences from Solrød Biogas A/S, at the first COASTAL Biogas conference on in Malmö, Sweden

Landtag Mecklenburg-Vorpommern, Wahlperiode 7, Drucksache 7/191, (13.02.2017): Kleine Anfrage des Abgeordneten Dr. Wolfgang Weiß, Fraktion DIE LINKE, Entsorgung oder Verwertung von Seegras und anderem Treibgut. (http://www.dokumentation.landtagmv.de/Parldok/dokument/38809/entsorgung-oder-verwertung-von-seegras-und-anderemstrandgut.pdf) [11-08-2019]

Lincke & Schwarz (2013): Kontinuierliche Vergärungsversuche in Liebetrau, in Pfeiffer, Thrän (Hrsg.) (2013): Messmethodensammlung Biogas

Lybæk, R. (2014): Development, Operation, and Future Prospects for Implementing Biogas Plants: The Case of Denmark, in Use, Operation and Maintenance of Renewable Energy Systems: Experiences and Future Approaches, M. A. Sanz-Bobi, Ed. Cham: Springer International Publishing, 2014, pp. 111-144.

Ministerium für Wirtschaft, Arbeit und Gesundheit (2018): Vollzugshinweise zur „Direkten Verwertung“ von Treibsel als Abfall auf landwirtschaftlichen Flächen in Mecklenburg-Vorpommern, Schwerin

Ministerium für Wirtschaft, Arbeit und Tourismus (2009): Energie aus Abfall in Mecklenburg-Vorpommern, Schwerin

Ptacnikova, R. (2013): Coastal marine biomass-to-energy potential in Lower Saxony

Schubert et al. (2015): Mapping and modeling eelgrass Zostera marina distribution in the western Baltic Sea

The contents of this publication are the sole responsibility of the author and can in no way be taken to reflect the views of the European Union, the Managing Authority or the Joint Secretariat of the Interreg South Baltic Programme 2014-2020. COASTAL Biogas project is funded by:

Interreg South Baltic

EUROPEAN UNION

European Regional Development Fund

Contact

Sebastian Foth
Rostock University, Department of Waste and Resource Management
✆ +49 (0)381.498-3405 | ✉ sebastian.foth2@uni-rostock.de
www.auf.uni-rostock.de/professuren/a-g/abfall-und-stoffstromwirtschaft/