Sustainable solutions for Sargassum inundations in Turks & Caicos

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A presentation for the technical webinar on Atlantic Sargassum organised by European Algae Biomass Organisation held on online 4th November 2020

SLIDE 1

Good afternoon, I am Dr John Milledge and I am part of the Algal Biotechnology Research Group at the University of Greenwich. We have been researching methods to exploit members of the genus Sargassum since I joined the team over seven years ago.

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Our initial interest was on *S. muticum,* an invasive species to the UK and Europe, which has been causing environmental and economic damage. Globally, invasive species cost 1.2 trillion Euros per year ~5 % of the world economy [1].

SLIDE 3

We, therefore, examined potential commercial opportunities to encourage harvesting and control as harvesting was expensive, and there was no industrial exploitation of the biomass resource. As part of the MacroBioCrude initially, we examined the potential of *S. muticum* as a fuel. We also investigated potential pharmaceutical and dental uses of *S. muticum* funded by the High-Value Chemical from Plants Network.

As we were studying application for the use of *S. muticum,* we became aware of the increasing problem of holopelagic Sargassum inundations on the beaches of the Gulf of Mexico and the Caribbean together with areas of coastal west Africa.

SLIDE 4

We received a number inquiries about our work on Sargassum and an invitation from the Caribbean Council in 2016 to speak at a conference on Sargassum in the British Virgin Islands; however, due other oversea commitment we were unable to attend. Nonetheless, this prompted us to review the current position on the uses and challenges of pelagic Sargassum, “Golden Tides: Problem or Golden Opportunity? [2] The Valorisation of Sargassum from Beach Inundations”. Several conversations were held with a variety of organisations on how the University of Greenwich could help examine the composition and use of pelagic Sargassum, but finding funding was the major stumbling block. Finally, Dr Debbie Bartlett and I, together with the Turks and Caicos Government obtained financing from Darwin PLUS in 2019 to examine “Sustainable solutions for Sargassum inundations in Turks & Caicos”.

Before we move on to examine our work on pelagic Sargassum inundation lets us first look at some of the key findings of our work on *S. muticum.*

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S. Muticum composition

	Moisture	Ash	N	C	H	S	O	Salt	HHV
	% total wt.	% dry weight						% Ash	kJ g^{-1} dw
March 2014	79.9	29.4	4.9	30.7	4.0	1.5	29.6		16.4
July 2015	85.5	33.1	3.6	30.1	4.2	0.8	28.1	46.1	12
June 2017	85.6	32.7	3.9	27	4.7	0.6	31.1	51.5	11.5

- High Moisture
- High Ash
- Varies seasonally

As with all seaweeds, *S. muticum* has a challenging composition for exploitation as a fuel it is high in moisture and rich in inorganic ash and the makeup varies seasonally [3].

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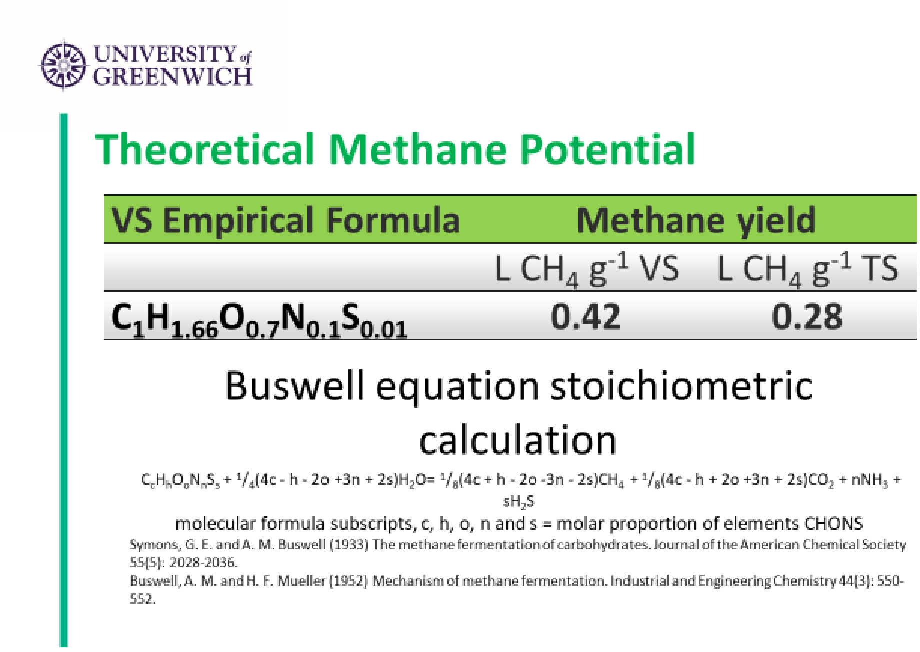
Biofuels

Method	Utilises entire organic biomass	Utilises wet biomass	Primary energy product
Direct combustion	✓	✗	Heat
Pyrolysis	✓	✗	Primarily solid by slow pyrolysis
Gasification	✓	✗ [b] (conventional)	Primarily Gas
Biodiesel production	✗	✗ [c]	Liquid
Hydrothermal treatments	✓	✓	Primarily Liquid
Bioethanol production	✗ [a]	✓	Liquid
Biobutanol production	✗ [a]	✓	Liquid
Anaerobic digestion	✓	✓	Gas

[a] Polysaccharides require hydrolysis to fermentable sugars. Some of the sugars produced from the breakdown of seaweed polysaccharides are not readily fermented; [b] Supercritical water gasification (SCWG) an alternative gasification technology can convert high moisture biomass; [c] No current commercial process for the wet trans-esterification of wet macroalgal biomass

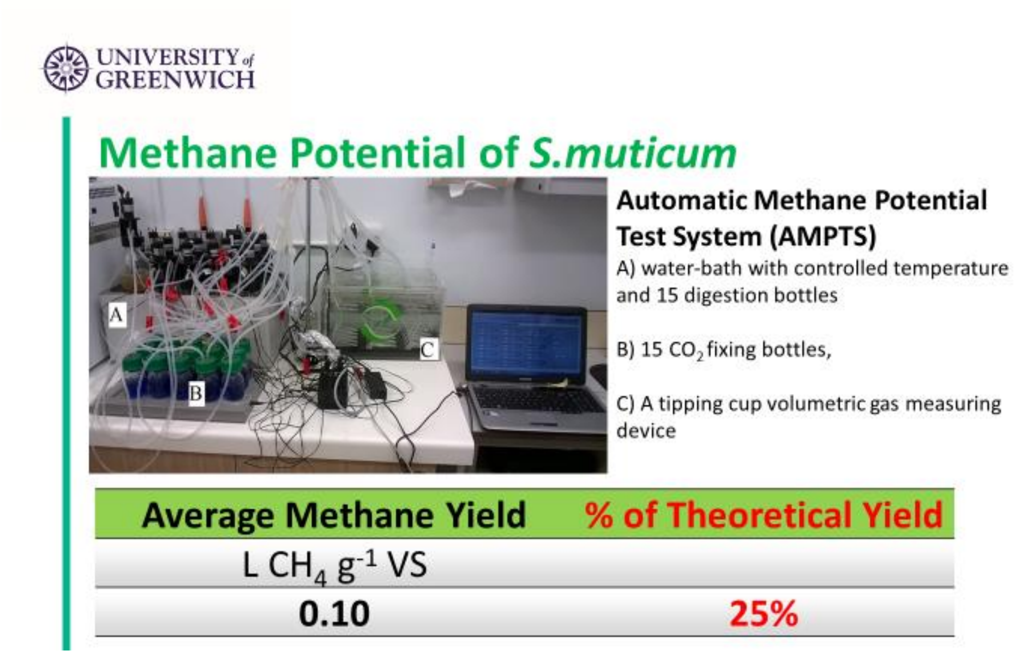
Methods which require drying may not be energetically viable. The amount of energy to dry Sargassum is nearly as high as the Higher Heating Value of the biomass [4]. Anaerobic digestion is generally the preferred method for wet biomass and can exploit the entire biomass [5,6].

SLIDE 7



The theoretical methane potential of S. muticum based on its empirical formula makes it a promising feedstock with a potential methane yield of 0.42 grams per gram of volatile solids (VS) [3].

SLIDE 8



However, the experimental methane potential was only around 25% of the theoretical.

There are several potential reasons for low practical yields from Sargassum.

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Considerable conjecture about low practical methane yields

- Inoculum
- Cell structure
- Resistant organic compounds
- Inhibition by anti-bacterial polyphenols and other compounds
- Salt and other inorganics
- Ammonia inhibition
- Halogens

However, two of the most important that we have examined are recalcitrant organic compounds and polyphenolics.

Seaweeds can be rich in hydrocolloids which can be difficult to breakdown, such as alginic acid [7-9].

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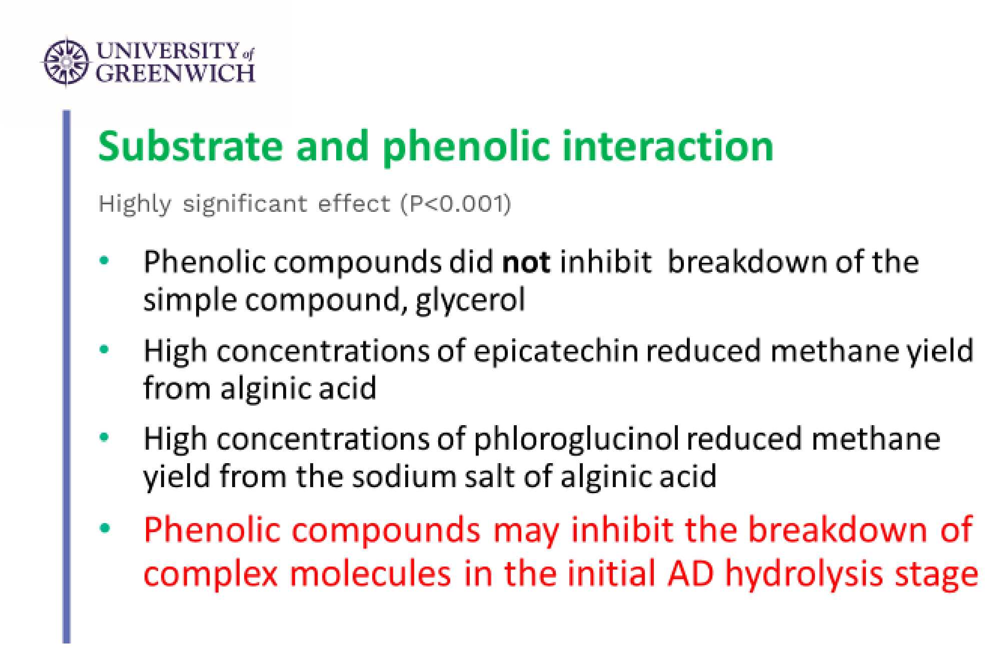
Alginic acid recalcitrant

Average Gas yield mL CH_4 g^{-1} substrate dw		
Alginic Acid Sodium Salt	Alginic Acid	Cellulose
76	73	183

The methane yield from both alginic acid and its sodium salt are only around 40% of cellulose [10].

Sargassum can be rich in phenolics containing up to 5% of the dry weight [11].

SLIDE 11



We carried out a study of examining the effect on methane yield of three simple, model phenolics, phloroglucinol, gallic acid and epicatechin on four model substrates, glycerol, Cellulose, Alginic acid and the Sodium salt of Alginic acid. A highly significant interaction was found between substrate and phenolics. Although none of the phenolics inhibited the breakdown of the simple compound glycerol, various phenolics appeared to inhibit the breakdown of more complex molecules [10]. Our PhD student Supattra Maneein is trying to identify the phenolic in *S. muticum* and has found the removal of phenolics by 70% methanol improves methane yield.

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I would now like to move on to our initial results of our work on the composition and methane potential of pelagic Sargassum from inundations on the beaches of Turks and Caicos.

Initial samples were collected by Dr Debbie Bartlett and two University of Greenwich MSc students from Shark Bay, South Caicos, Turks and Caicos in June 2019 under a Turks and Caicos Scientific Research Permit and immediately shipped chilled to our Medway campus. We received four samples collected nearshore:

a) a mixed sample
b) *S. natans VIII*
c) *S. natans I*
d) *S. fluitans*

Fresh samples were analysed for moisture and ash content, and a fresh mixed was investigated for methane potential using a CJC methane potential tester. The remaining samples were then freeze-dried for further analysis.

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High in moisture, ash & salt
Low in calories

	% Moisture (ar)	% Ash (dw)	% Ts (ww)	% VS (ww)	% Salt (ww)	HHV kJ g^{-1}
Mixed 'Sargassum'	82.0%	46.9%	18.0%	9.6%	2.7%	9.4
S. natans VIII	86.5%	34.3%	13.5%	8.9%	2.6%	10.2
S natans I	87.4%	35.7%	12.6%	8.1%	2.9%	10.2
S fluitans	86.3%	33.6%	13.7%	9.1%	2.6%	10.3

All the fresh samples were high in moisture ash and salt and low in calories. The unsorted mixed inundation sample was significantly different, being lower in calories and moisture but higher in ash.

SLIDE 14

Difficult to digest – high fibre

	Ash	Lipid	Total AAs	Total Fibre	Carb'		Indigestible	Digestible
Mixed 'Sargassum'	46.9%	3.9%	4.2%	33.3%	11.7%		80.3%	19.7%
S. natans VIII	34.3%	3.6%	3.0%	37.4%	21.8%		71.7%	28.3%
S natans I	35.7%	4.5%	3.8%	37.0%	19.0%		72.7%	27.3%
S fluitans	33.6%	4.6%	3.3%	31.2%	27.4%		64.8%	35.2%

All the samples were rich in fibre. This, together with the high ash, means that 65-80% of the solids of pelagic Sargassum is indigestible or difficult to breakdown in the gut or by AD. The protein contents are towards the low end of the protein content (3–16%) reported for brown seaweeds and pelagic Sargassum [12-14]. However, the amino acid profile compares favourably with the ‘indispensable amino acid’ profile recommended by the World Health Organisation (WHO) and does not appear to be lacking in any amino acid. The lipid contents were relatively comparable across the four samples and similar to those previously reported for brown seaweed [12] but above those for pelagic Sargassum [14,15]. The most prevalent fatty acid was palmitic acid, which may play a role in controlling the ‘biofouling’ of the fronds of Sargassum [16-18].

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Arsenic could be problematic

		Mixed	*S. natans VIII*	*S. natans I*	*S. fluitans*
Aluminium	mg kg⁻¹ dw	37.5	16.21	21.48	28.09
Arsenic	mg kg⁻¹ dw	123.69	20.94	29.76	26.25
Cadmium	mg kg⁻¹ dw	0.13	0.09	0.12	0.12
Calcium	mg kg⁻¹ dw	70305.77	26019.69	28879.26	33196.4
Chromium	mg kg⁻¹ dw	<0.3	0.36	ND	0.43
Copper	mg kg⁻¹ dw	2.51	1.25	2.71	2.91
Iron	mg kg⁻¹ dw	3811.37	81.58	998.56	262.02
Lead	mg kg⁻¹ dw	0.26	0.48	0.28	0.37
Magnesium	mg kg⁻¹ dw	12053.19	15092.59	16546.71	16320.64
Manganese	mg kg⁻¹ dw	30.15	<3	<3	<3
Mercury	mg kg⁻¹ dw	0.01	0	0.01	0.01
Phosphorus	mg kg⁻¹ dw	500.65	138.3	222.15	214.28
Potassium	mg kg⁻¹ dw	69359.39	7442.57	12509.16	7771.73
Zinc	mg kg⁻¹ dw	5.81	26.49	30.88	35.64

Samples collected from Shark Bay, South Caicos, Turks and Caicos (21.491N, 71.503W) June 2019

There have been concerns concerning the use of Sargassum, as seaweeds can bioaccumulate metals at concentrations many times above the levels found in the surrounding seawater [19-21]. Our results from the metal and metalloid analyses are generally in the range reported by Rodríguez-Martínez*, et al.* [22] in a recent study on the concentrations of fourteen different elements in pelagic Sargassum collected from the Mexican Caribbean coast. Arsenic levels found both in this study and by Rodríguez-Martínez, et al. [22] are above many regulatory limits. Inorganic arsenic is more toxic than organic arsenic, and although many seaweeds accumulate arsenic as less noxious arsenosugars, some species of Sargassum can have up to 80% of their arsenic content as the highly toxic inorganic form [23,24]. Despite these high levels, there is a lack of information on arsenic speciation in seaweed, and in pelagic Sargassum in particular. More work in this area is required, and care should be taken in the use of pelagic Sargassum as fertiliser and feed supplement and until this work is undertaken. Nonetheless, the high ash content of Sargassum could provide minerals and trace elements that are beneficial in both fertiliser and animal feed [14,25-27]. The limited calorific value of Sargassum and limited protein levels, despite an excellent amino acid profile, could limit its potential as a feed.

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Low Methane yields

Strong negative correlations with both arsenic and phenolics

	Methane Potential mL CH_4 g^{-1} VS		
	Actual	Theoretical	Actual as % Theoretical
Mixed 'Sargassum'	-24	496	-5%
S. natans VIII	145.1	395	37%
S. natans I	65.8	392	17%
S. fluitans	112.7	392	29%

This appears to be the first study to have attempted to establish the methane potential of 'fresh' pelagic Sargassum. Freeze-drying can not only reduce the mass to be transported but can also preserve biological materials with minimum damage from heat. Our research in this study and other unpublished results at the have found that there is no statically significant effect from freeze-drying on methane yields. Thus, freeze-drying appears a suitable technique for preserving pelagic Sargassum for transport for methane potential testing. The reduced weight will also reduce transport costs. A freeze-drier has been installed at the Centre for Fields on Turks and Caicos that will allow us to study seasonal variations and changes in Sargassum stranded on the beach.

The methane potentials from all the substrates were considerably below the theoretical potential. The mixed sample had a methane potential that was not significantly different from the blank. However, the MP of a combination of *S. natans VIII, S. natans I* and *S. fluitans* in a ratio typically found in the waters of Turks and Caicos was very similar to that predicted from the MPs of the individual species. Thus, there does not appear to be a synergistic or antagonist interaction between the species on MP. It seems that inhibitors to methane production must be either present or present at higher levels in the mixed unsorted sample than in individual pelagic species. The composition of the 'mixed Sargassum' mats can be substantially different from the individual species, and methane inhibitors may come from other organisms and materials present in the unsorted samples.

There were strong negative correlations with both arsenic and phenolic content with methane potential. Although a high degree of correlation does not confirm causality, these finds agree with the published literature and our work on *S. muticum*. Arsenic can be highly inhibitory to anaerobic digestion AD [28,29]. Phenolics have been implicated as the inhibitor of AD in several seaweed studies [10,30-35]. Although the information is still somewhat limited, especially on Sargassum, phenolics appear to be a significant factor in the low methane yield from Sargassum and especially the mixed mats where the phenolic level was highest.

The exploitation of Sargassum, and especially unsorted mixed mats, for biogas, would appear to be very challenging. Sargassum may need to be pre-treated before AD or co-digested with other waste biomass to increase yield.

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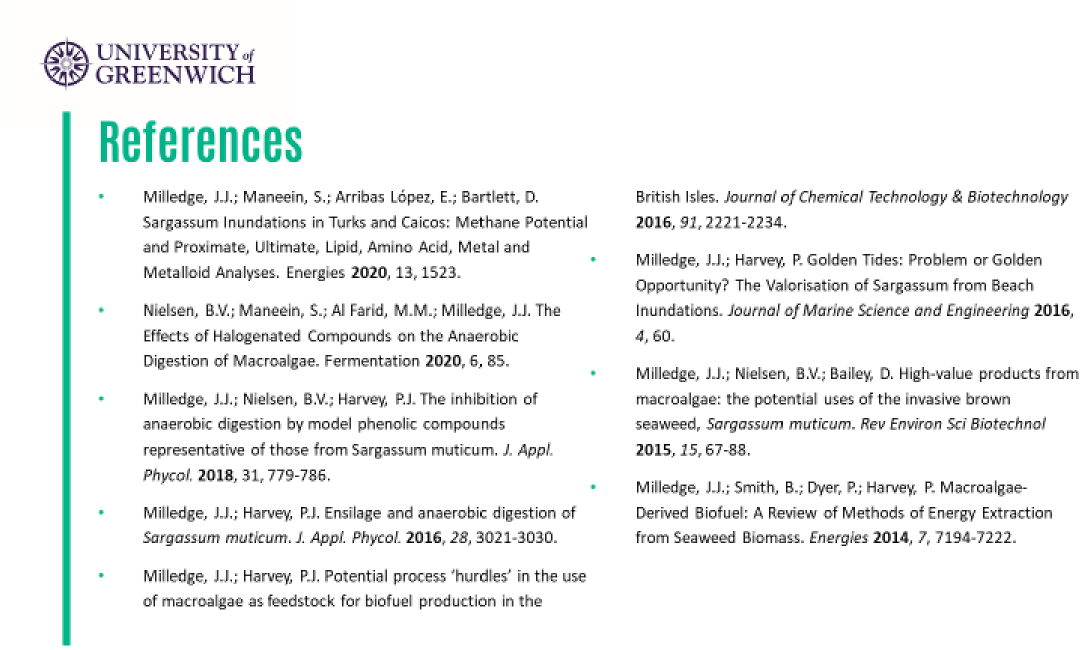
We are expecting to be able to analyse more samples from Turks and Caicos over the coming months to provide further detail on the composition of Sargassum and implications on its use as a source of biogas, fertiliser and feed supplements.

SLIDE 18



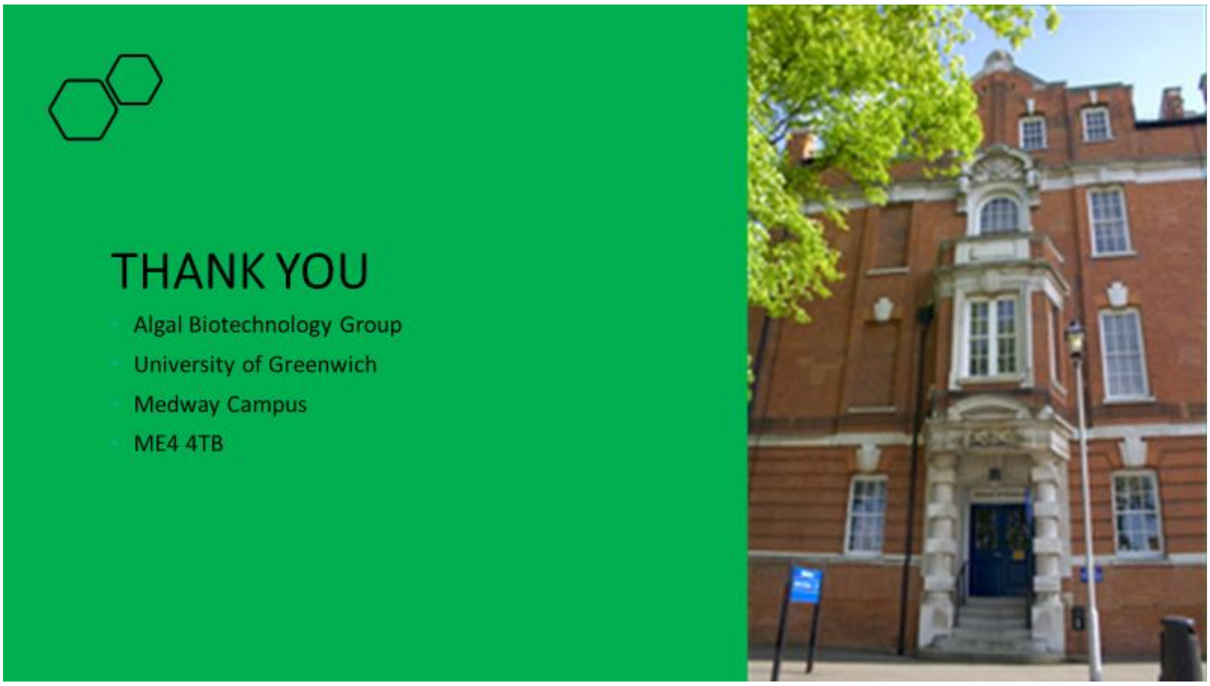
Here are some of the references to our work. I hope that these slides will be available after this conference. I also have a transcript of my talk with citations, which I also hope to make public.

SLIDE 19

Finally, I would like to thank all my colleagues and collaborators together with the Darwin Fund for funding our work on Turks and Caicos and the other funders of our work on Sargassum.

Thank you

SLIDE 21



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