High Value Products from Seaweed

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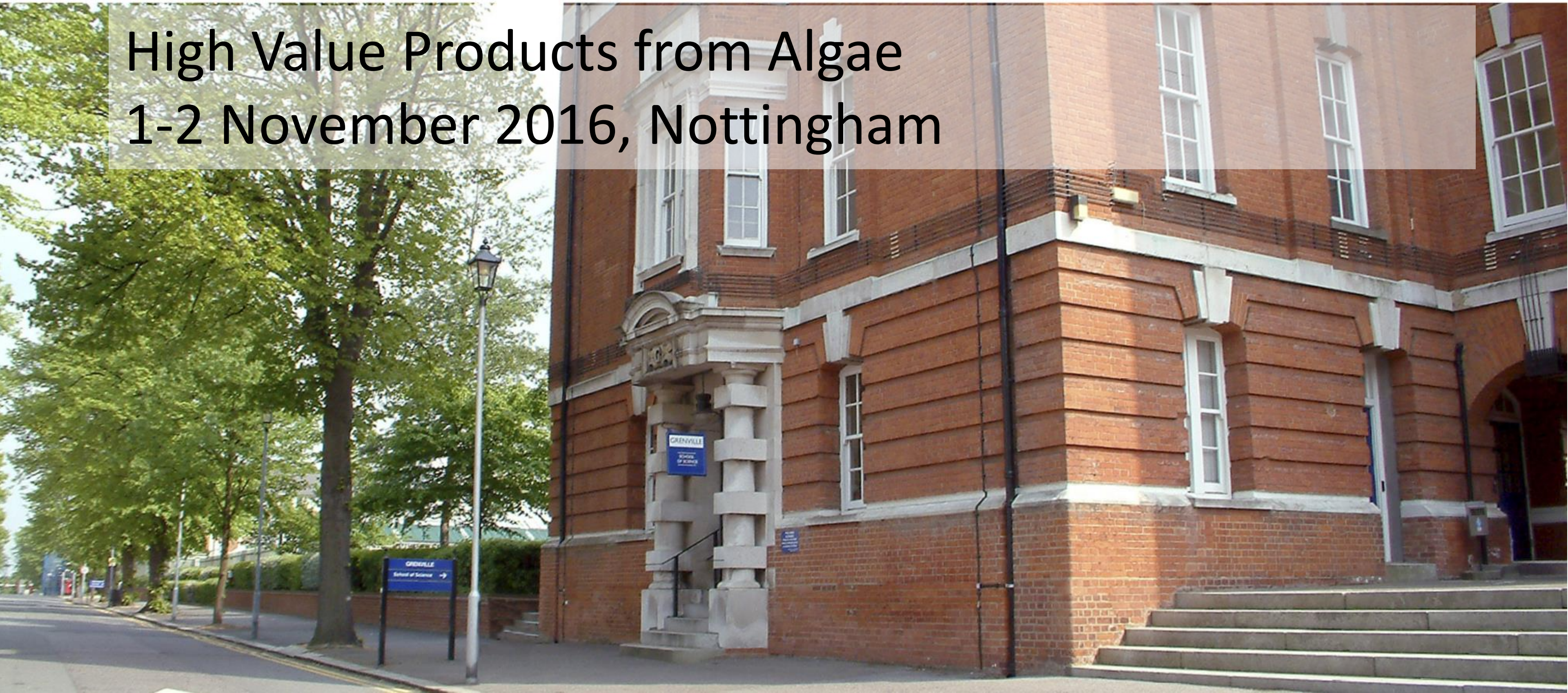
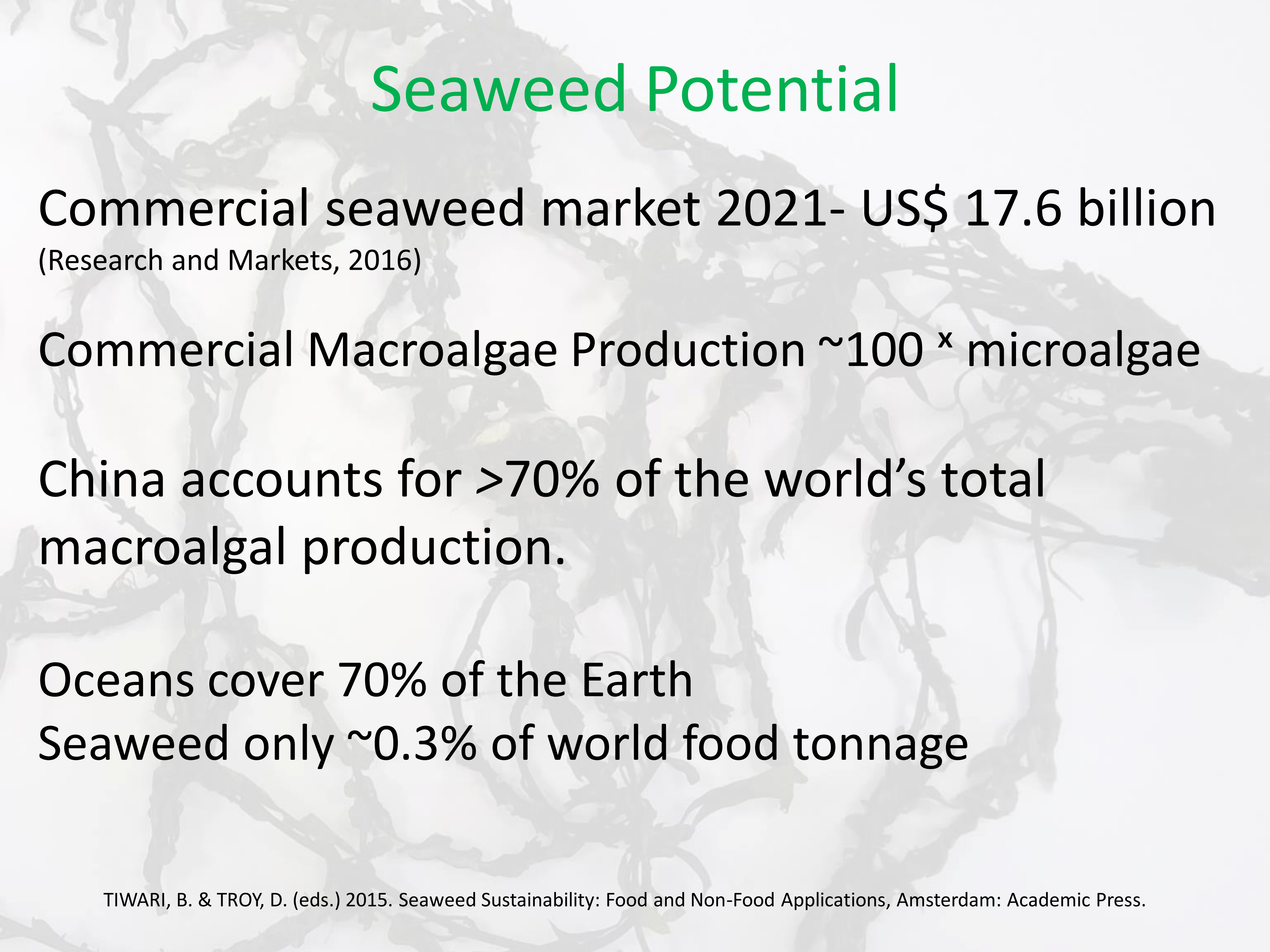


High Value Products from Algae
1-2 November 2016, Nottingham



Seaweed Potential

Commercial seaweed market 2021- US$ 17.6 billion
(Research and Markets, 2016)

Commercial Macroalgae Production ~100 ^{x} microalgae

China accounts for >70% of the world's total macroalgal production.

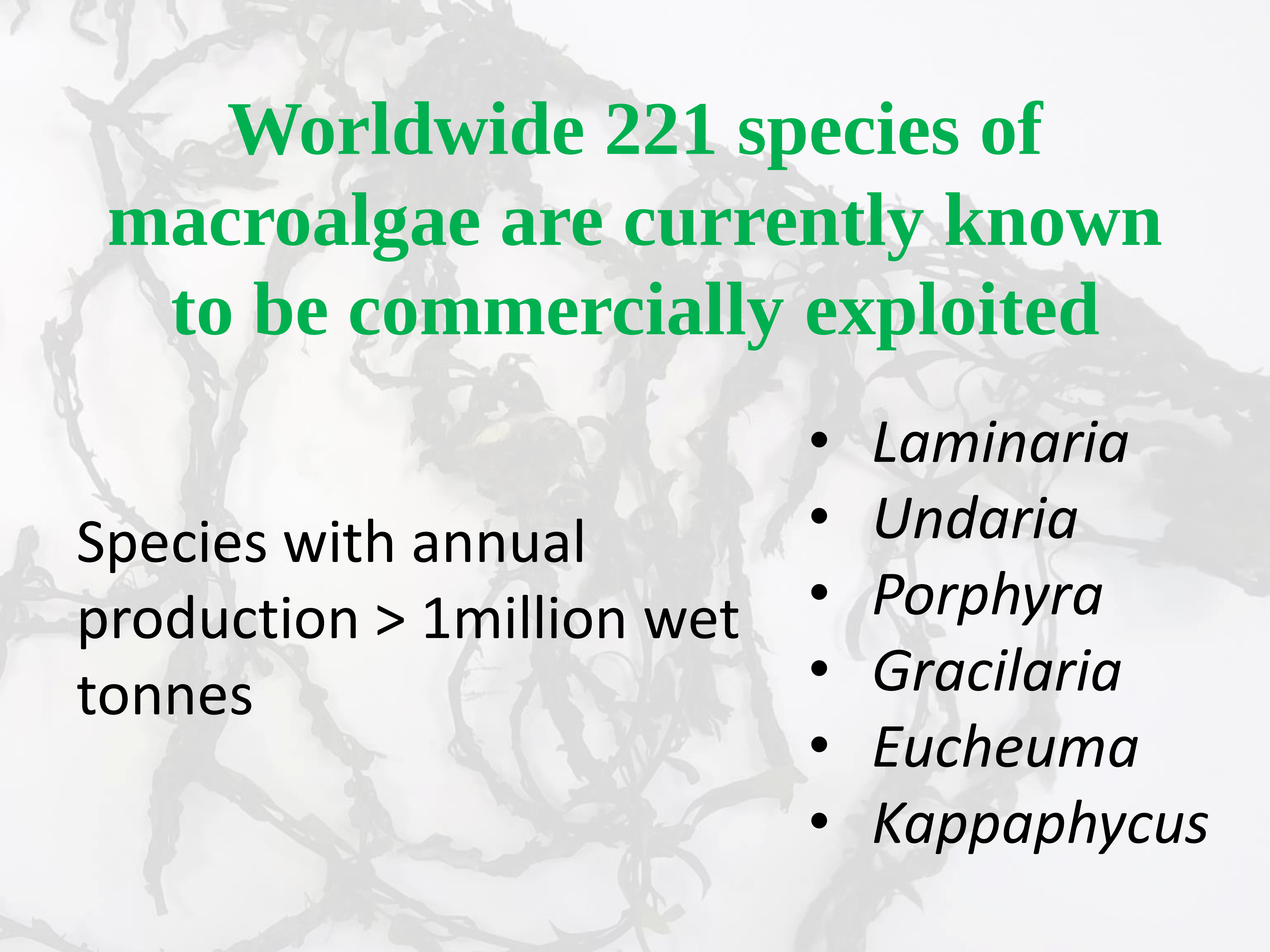
Oceans cover 70% of the Earth
Seaweed only ~0.3% of world food tonnage

TIWARI, B. & TROY, D. (eds.) 2015. Seaweed Sustainability: Food and Non-Food Applications, Amsterdam: Academic Press.

UK Commercial seaweed

- 27 Seaweed-related businesses
- 16 use UK harvested seaweed
- Primarily for food and condiments

CAPUZZO, E. & MCKIE, T. 2016. Seaweed in the UK and abroad – status, products, limitations, gaps and CEFAS role. Lowestoft: Centre for Environment, Fisheries & Aquaculture Science.



Worldwide 221 species of macroalgae are currently known to be commercially exploited

Species with annual production > 1million wet tonnes

- *Laminaria*
- *Undaria*
- *Porphyra*
- *Gracilaria*
- *Eucheuma*
- *Kappaphycus*

Commercially harvested seaweed in Ireland

Species	Annual Harvest (tonnes)
Ascophyllum nodosum	25,000
Fucus serratus	200
Palmaria palmata	<100
Chondrus crispus / Mastocarpus stellatus	<100
Laminaria digitata	<150
Himanthalia elongata, Saccharina latissima, L. hyperborea, *Ulva sp., Porphyra sp., F. vesiculosus, Alaria esculenta etc.*	<10

EDWARDS, M. & WATSON, L. 2011. Aquaculture Explained Cultivating Laminaria digitata. Galway: Irish Sea Fisheries Board

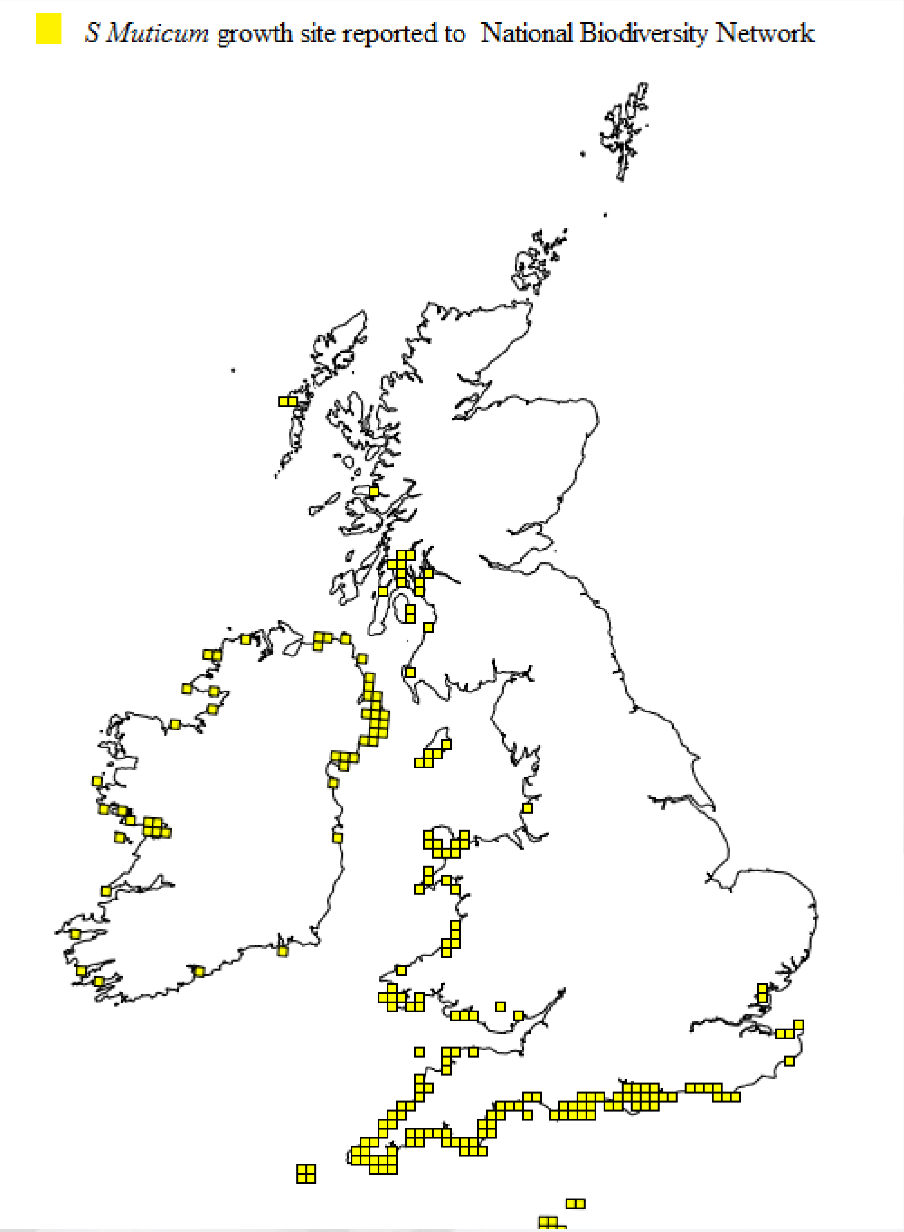
Sargassum muticum (Japanese Wireweed)

- Found in Europe early 1970s.
- Now found from Norway to Portugal

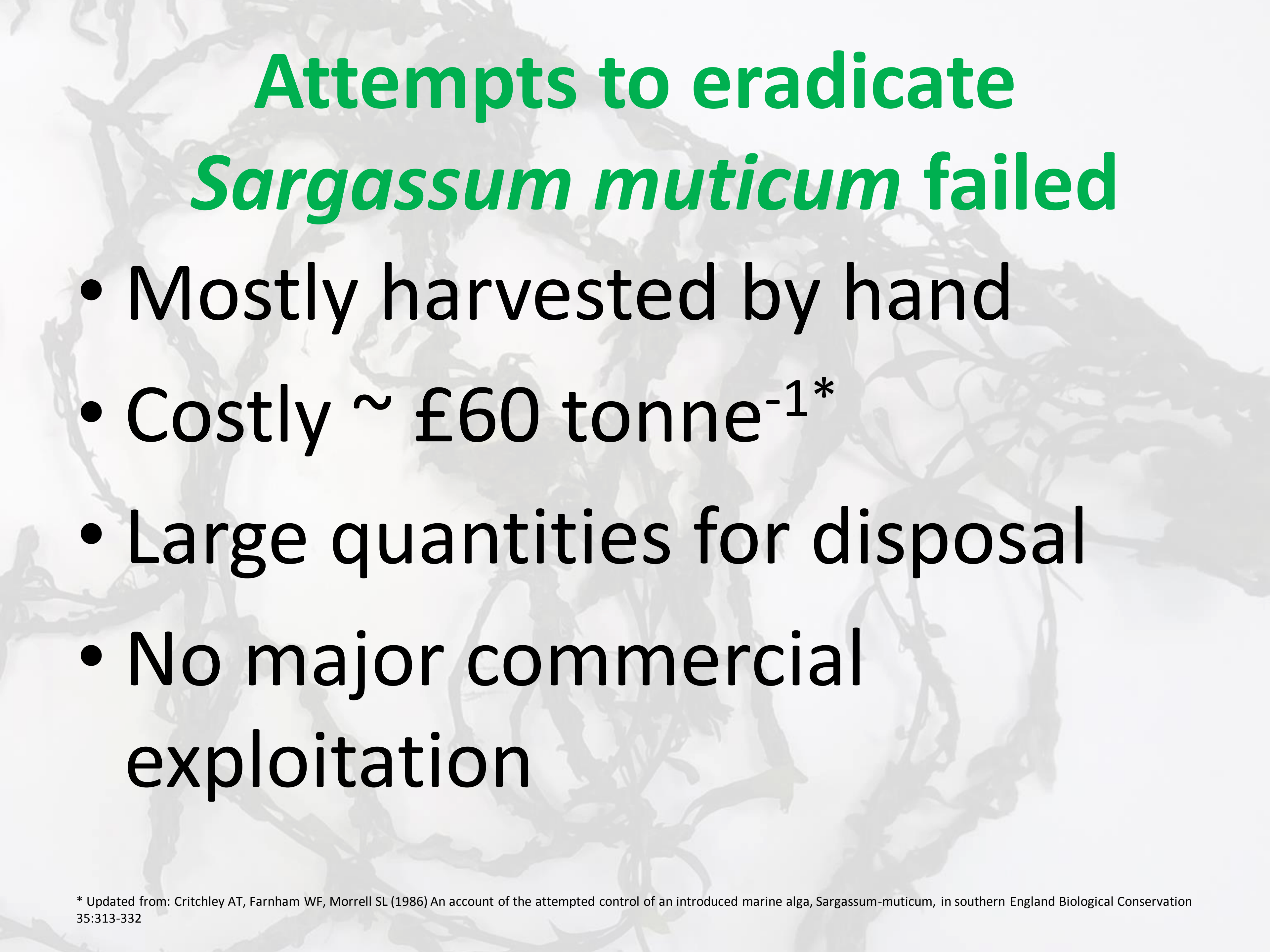
S. muticum has spread along the south-coast and around the British Isles

- Very invasive
- Most 'successful' invasive, rate of spread in UK
- Higher growth rate

  >10 x *Ascophyllum nodosum*
- High priority EU's Water Framework Directive



Courtesy of National Biodiversity Network



Attempts to eradicate *Sargassum muticum* failed

- Mostly harvested by hand
- Costly ~ £60 tonne^{-1}*
- Large quantities for disposal
- No major commercial exploitation

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* Updated from: Critchley AT, Farnham WF, Morrell SL (1986) An account of the attempted control of an introduced marine alga, Sargassum-muticum, in southern England Biological Conservation 35:313-332

theguardian

Caribbean-bound tourists cancel holidays due to foul-smelling seaweed
Monday 10 August 2015

Massive inundations of pelagic Sargassum known as Golden-tides on the beaches of the Caribbean, Gulf of Mexico and West Africa

The Economist

Caribbean resorts
Plaguing paradise
Smelly piles of seaweed are ruining holidays
Aug 29th 2015 |

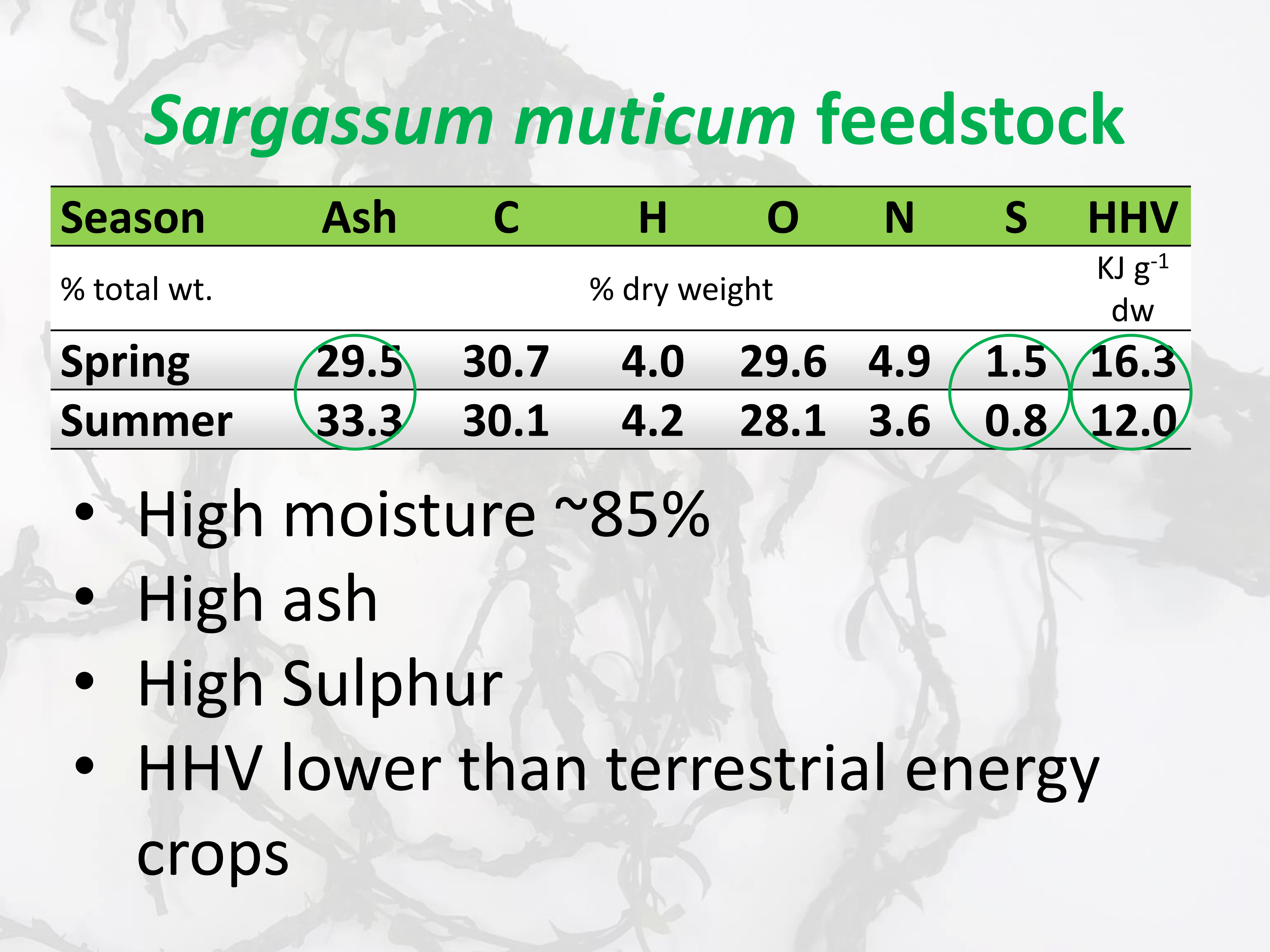
Photographs courtesy of Kelly (Robinson) de Schaun

Food, Feed & Fertiliser

Abalone-farming courtesy Namibian Sun

“Gathering Seaweed” by Harold Harvey, courtesy of David Messum Fine Art

Potential high levels of heavy metals ?



Sargassum muticum feedstock

Season	Ash	C	H	O	N	S	HHV
% total wt.			% dry weight				KJ g^{-1} dw
Spring	**29.5**	**30.7**	**4.0**	**29.6**	**4.9**	**1.5**	**16.3**
Summer	**33.3**	**30.1**	**4.2**	**28.1**	**3.6**	**0.8**	**12.0**

- High moisture ~85%
- High ash
- High Sulphur
- HHV lower than terrestrial energy crops

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

Pyrolysis

- Pyrolysis is the thermal decomposition of the organic component of dry biomass by heating in the absence of air.
- The distribution between solid, liquid and syngas depends on the biomass and the pyrolysis temperature and time

Slow Pyrolysis of *Sargassum Muticum*

	% of original DW	HHV
		kJ g^{-1}
Biochar	**67.6%**	**15.7**
Syngas	**16.5%**	**2.9**
Biocrude	**11.7%**	**15.6**
Tar 'hold-up'	**4.4%**	**30.1**

Slow pyrolysis (<400 °C) produces more solid char

Energy yield 98 %

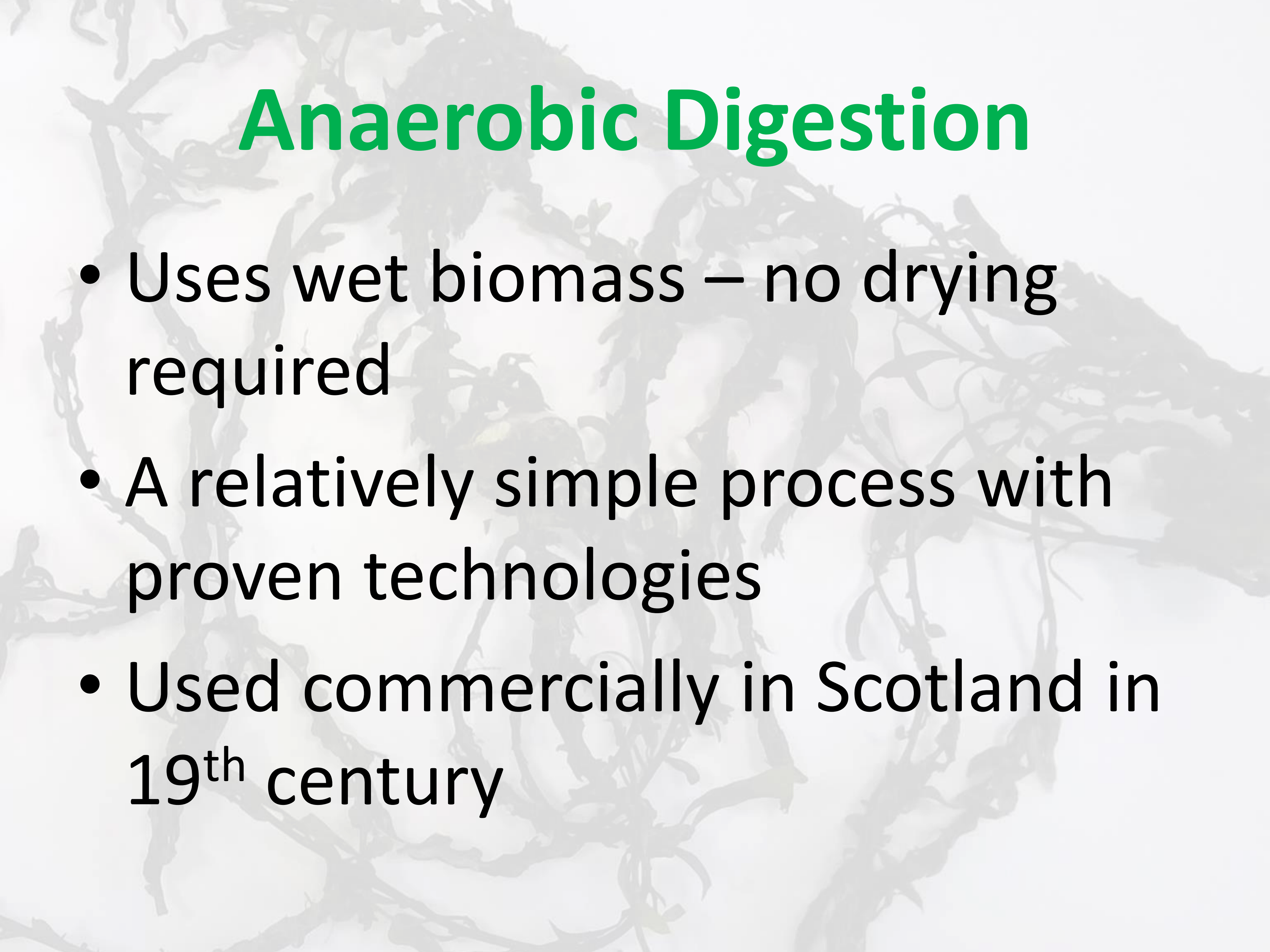
Energy Balance Pyrolysis of *Sargassum Muticum*

	MJ
Energy to raise temp 1kg of dry seaweed by 400 °C	**0.5**
Energy in Biocrude & Syngas	**2.9**
Energy in all Pyrolysis Products	**14.9**
Heat energy to produce 1kg dry seaweed	**10.4**

Sufficient energy in the biocrude and syngas to power pyrolysis

70% of energy produced

Insufficient energy within the seaweed for drying



Anaerobic Digestion

- Uses wet biomass – no drying required
- A relatively simple process with proven technologies
- Used commercially in Scotland in 19th century

Theoretical Methane Potential

VS Empirical Formula	Methane yield	
	L CH_4 g^{-1} VS	L CH_4 g^{-1} TS
$C_1H_{1.66}O_{0.7}N_{0.1}S_{0.01}$	**0.42**	**0.28**

Buswell equation stoichiometric calculation

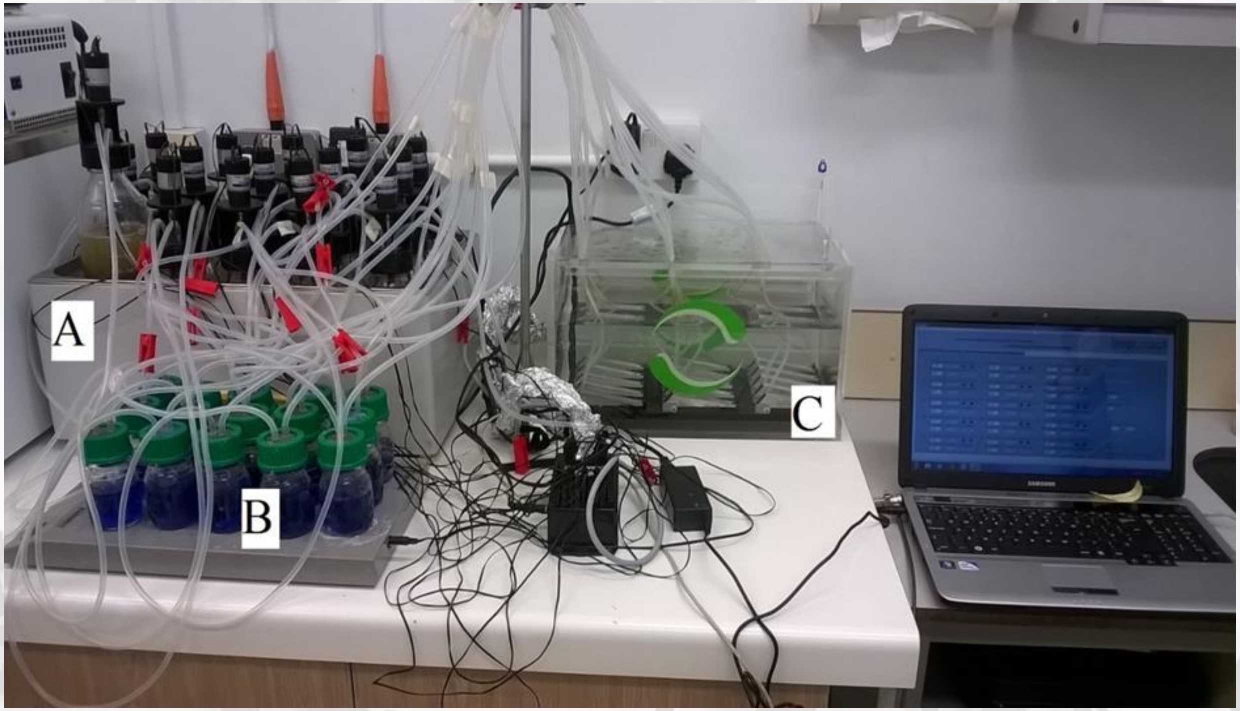
$$C_cH_hO_oN_nS_s + {}^1/_4(4c - h - 2o + 3n + 2s)H_2O = {}^1/_8(4c + h - 2o - 3n - 2s)CH_4 + {}^1/_8(4c - h + 2o + 3n + 2s)CO_2 + nNH_3 + sH_2S$$

molecular formula subscripts, c, h, o, n and s = molar proportion of elements CHONS

Symons, G. E. and A. M. Buswell (1933) The methane fermentation of carbohydrates. Journal of the American Chemical Society 55(5): 2028-2036.

Buswell, A. M. and H. F. Mueller (1952) Mechanism of methane fermentation. Industrial and Engineering Chemistry 44(3): 550-552.

Methane Potential



Automatic Methane Potential Test System (AMPTS)

A) water-bath with controlled temperature and 15 digestion bottles

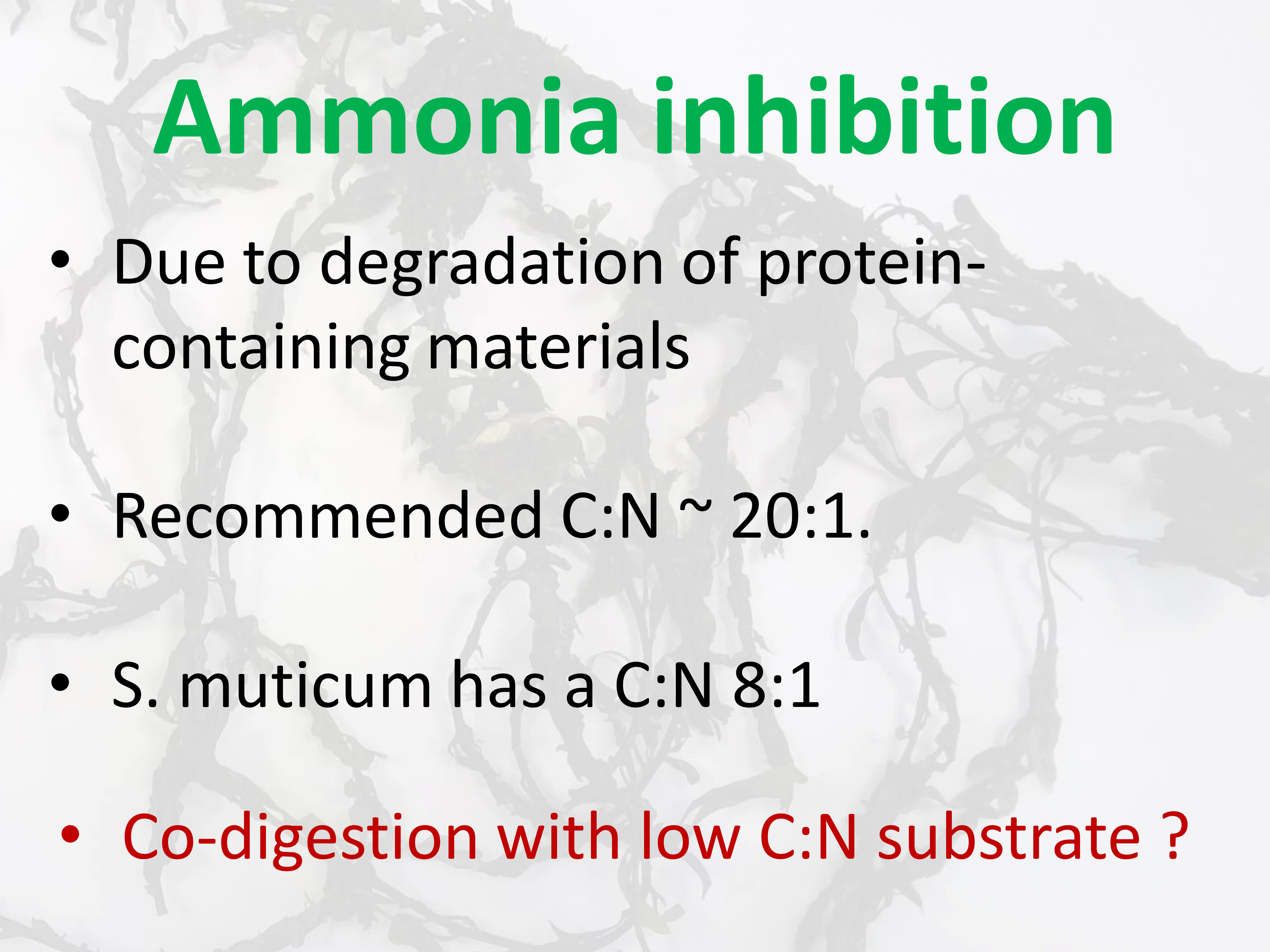
B) 15 CO2 fixing bottles,

C) A tipping cup volumetric gas measuring device

Average Methane Yield	% of Theoretical Yield
L CH_4 g^{-1} VS	
0.10	**25%**

Considerable conjecture about low practical methane yields

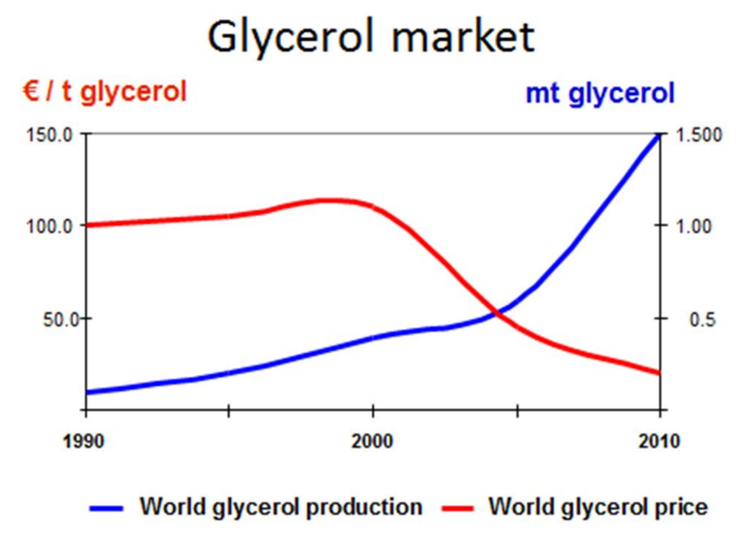
- Inoculum
- Cell structure
- Resistant organic compounds
- Inhibition by anti-bacterial polyphenols and other compounds
- Salt and other inorganics
- Ammonia inhibition



Ammonia inhibition

- Due to degradation of protein-containing materials
- Recommended C:N ~ 20:1.
- S. muticum has a C:N 8:1
- Co-digestion with low C:N substrate ?

Co-digestion with Crude Glycerol



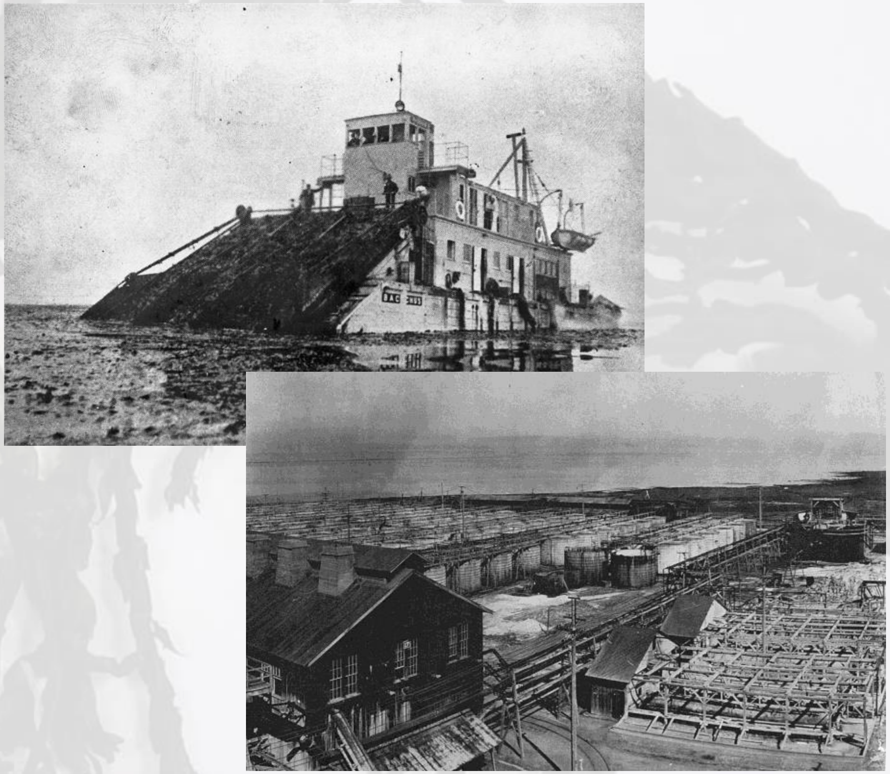
Co-digestion with Crude Glycerol

	Ave Methane Yield	% of Theoretical Yield
	L CH_4 g^{-1} VS	
Crude Glycerol	**0.26**	**46%**
Sargassum muticum	**0.07**	**17%**
50% Crude Glycerol & *S. muticum*	**0.21**	**43%**

Co-digestion increased biogas yield by 27%

Maintaining Year Round Supply

- Harvesting is seasonal
- Need to preserve and store for a continuous supply



Little research on how to preserve seaweed biomass year round in order to satisfy continuous process demand

“An understanding of ensiling of seaweed is absolutely crucial for a substantial seaweed biofuel industry”

Herrmann C, FitzGerald J, O'Shea R, Xia A, O'Kiely P, Murphy JD (2015) Ensiling of seaweed for a seaweed biofuel industry Bioresour Technol 196:301-313

Ensilage

- Routinely used for the storage of forage for animal feed
- Lactic acid fermentation under anaerobic conditions converts water-soluble carbohydrates into organic acids, mainly lactic acid.
- Initiated by naturally-present bacteria
- pH decreases and the moist crop is preserved

Ensiled seaweed composition

	Moisture	C	H	O	N	S	Ash	Salt	HHV
	% total wt.			% dry weight				% of ash	KJ g^{-1} dw
Unensiled	**85.4**	**30.1**	**4.2**	**28.1**	**3.6**	**0.8**	**33.3**	**46.1**	**12.05**
Ensiled whole	**85.5**	**30.0**	**4.2**	**29.3**	**3.3**	**<0.1**	**33.1**	**43.6**	**12.13**
Ensiled chopped	**85.2**	**29.4**	**3.9**	**29.8**	**3.5**	**<0.1**	**33.3**	**45.9**	**12.36**

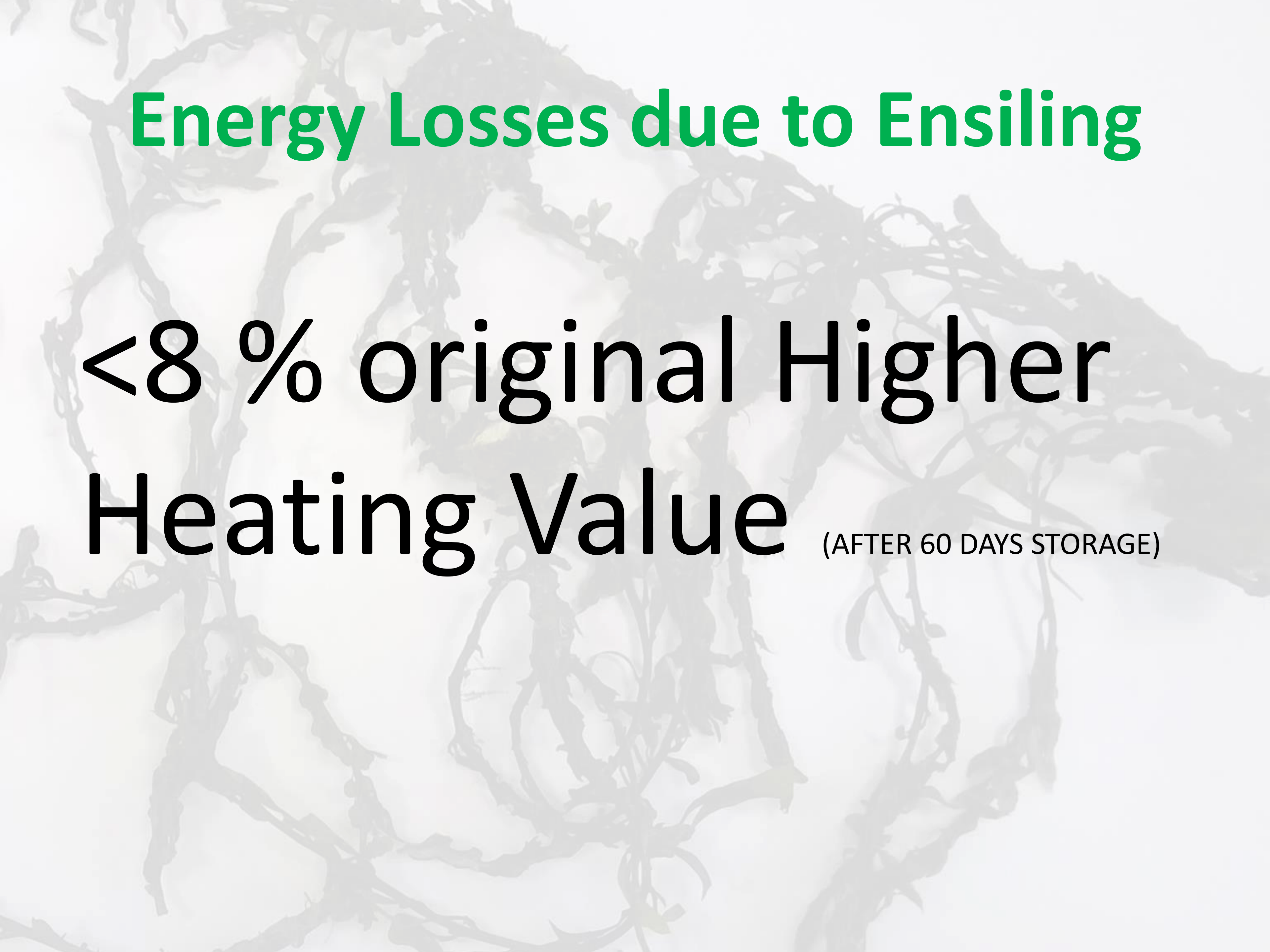
- No sig difference in CHON, ash and HHV
- Ensiling results in a significant reduction in salt
- Chopping reduces salt loss
- Ensiling results in virtual total loss of organic sulphur

Leachate composition

	Moisture	VS	Ash	Salt	w/w % of feedstock
	% total wt.	% dw		% of ash	
Ensiled whole leachate	**92.3**	**38.8**	**61.2**	**43.6**	**7.8**
Ensiled chopped leachate	**92.2**	**49.2**	**50.8**	**45.9**	**3.2**

- Leachate losses low 3.2-7.8% wet weight
- Leachate is mainly water, ash and salt
- VS losses low 2.8-8.4% of original VS
- Chopping reduces overall leachate losses

Energy Losses due to Ensiling



<8 % original Higher Heating Value (AFTER 60 DAYS STORAGE)

Effect of Ensilage on CH_4 Yield

	Methane production	
	L CH_4 g^{-1} VS	
	Average	StdV
Untreated	**0.10**	**0.05**
Ensiled whole	**0.11**	**0.08**
Chopped prior to ensiling	**0.06**	**0.01**

No statistically significant effect on methane yields

UK Roadmap for Algal Technologies

Main opportunity in the UK are In the short to medium term

High value products

- Condiments and premium sea vegetables
- Hydrocolloids
- Bioactives

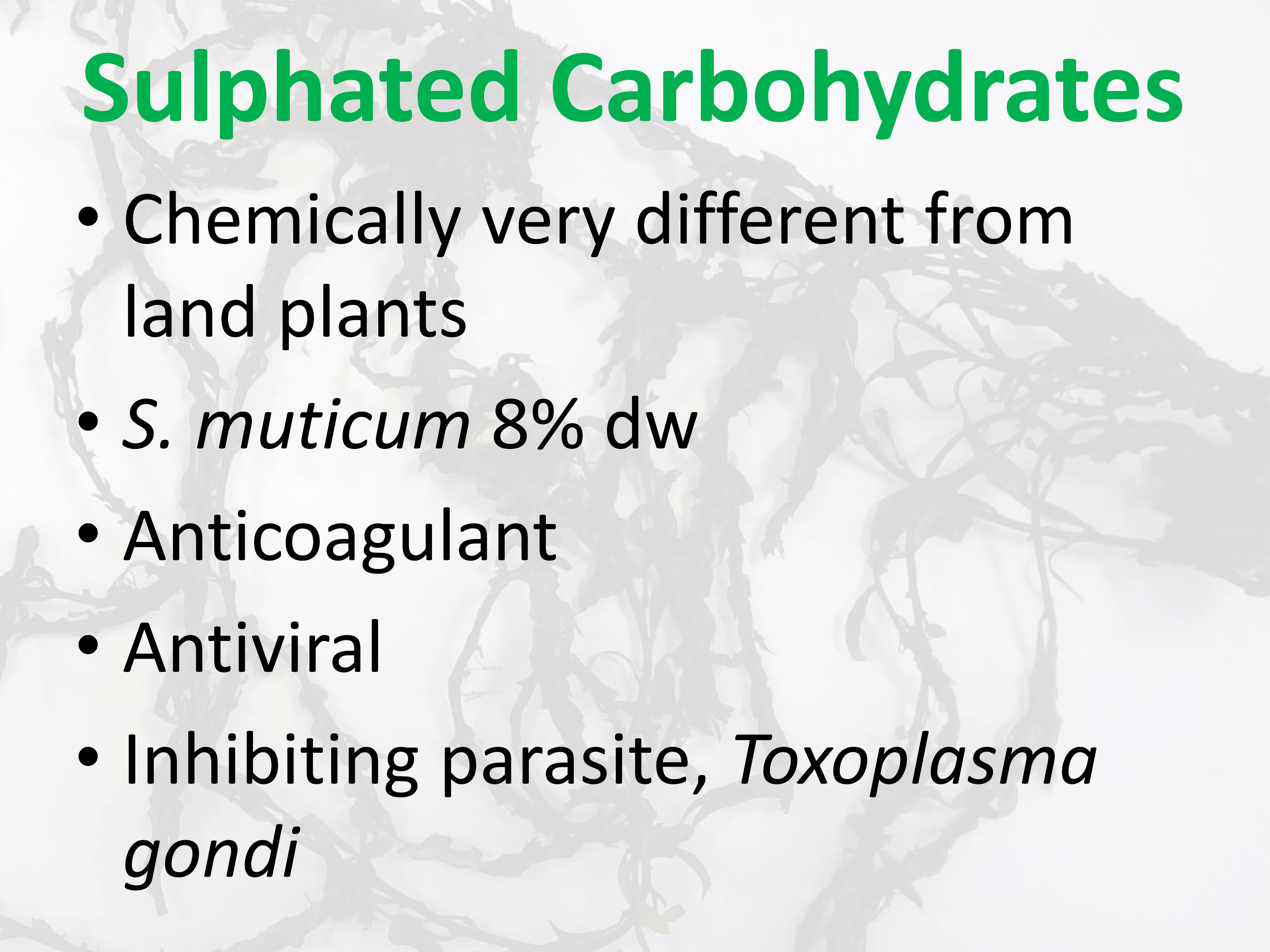
SCHLARB-RIDLEY, B. & PARKER, B. 2013. A UK roadmap for algal technologies. NERC-TSB.

Alginates

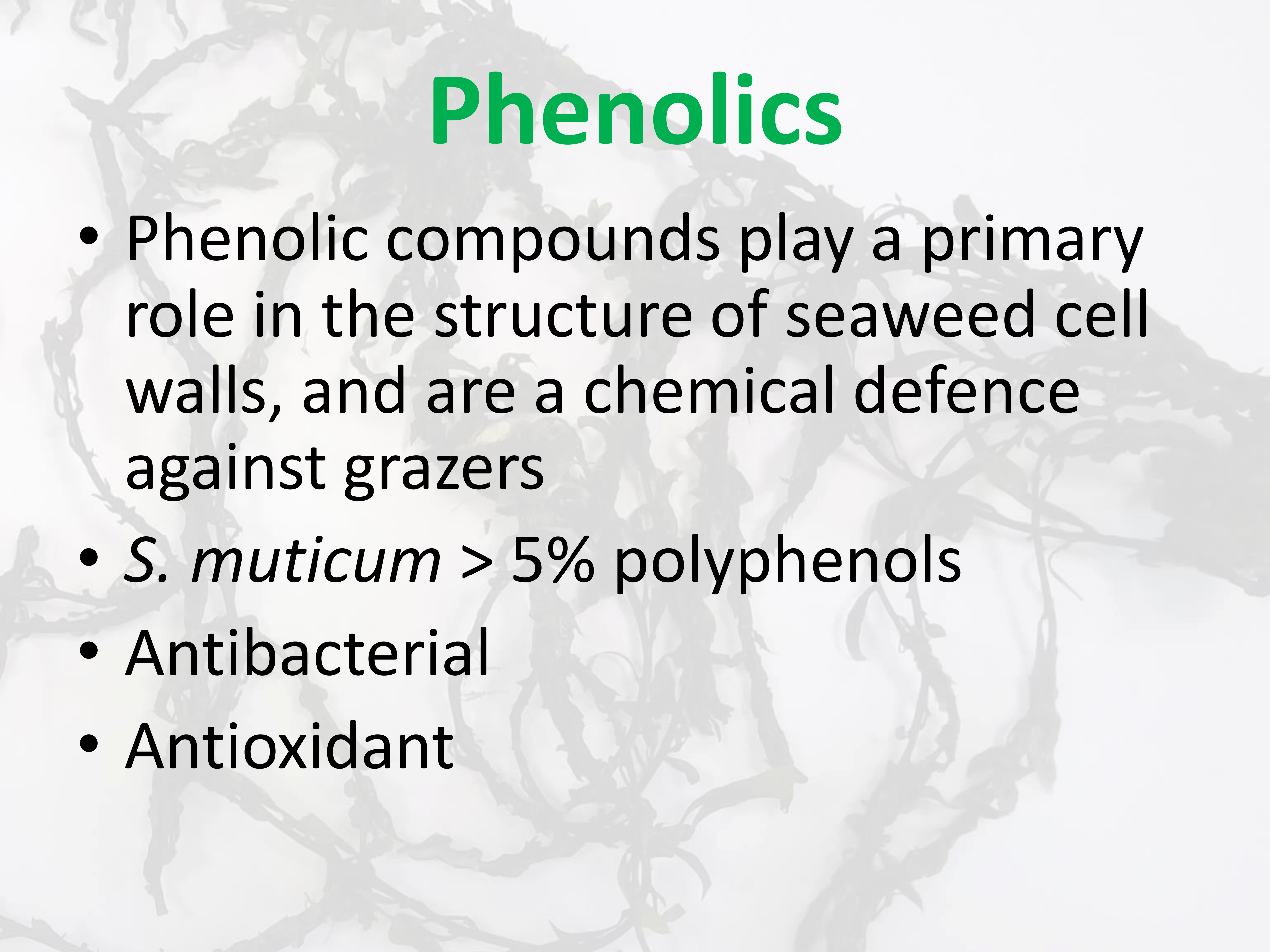
- Major component of the cell-wall of brown algae
- Worldwide annual production 30,000 tonnes
- Yield is relatively low, 5-11% from *S. Muticum* compared to 16 -30% for commercially exploited brown algae

Critchley AT *et al*.(1986) An account of the attempted control of an introduced marine alga, *Sargassum-muticum*, in southern England Biological Conservation 35:313-332
Gonzalez-Lopez N *et al*.((2012) Hydrothermal fractionation of *Sargassum muticum* biomass J Appl Phycol 24:1569-1578
Liu F *et al*.((2013) Intraspecific genetic analysis, gamete release performance, and growth of *Sargassum muticum* (Fucales, Phaeophyta) from China Chin J Ocean Limnol 31:1268-1275
Rehm BHA (ed) (2009) Alginates: Biology and Applications. Microbiology Monographs, , vol 13. Springer, Heidelberg.
Zhao FJ *et al*.((2008) Genetic structure analysis of natural *Sargassum muticum* (Fucales, Phaeophyta) populations using RAPD and ISSR markers J Appl Phycol 20:191-198

Sulphated Carbohydrates



- Chemically very different from land plants
- *S. muticum* 8% dw
- Anticoagulant
- Antiviral
- Inhibiting parasite, *Toxoplasma gondi*



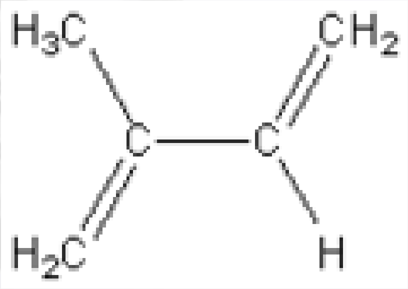
Phenolics

- Phenolic compounds play a primary role in the structure of seaweed cell walls, and are a chemical defence against grazers
- *S. muticum* > 5% polyphenols
- Antibacterial
- Antioxidant

Terpenes & Terpenoids

50,000 have been isolated from algae, terrestrial, and fungi

Predominate new compounds isolated from brown seaweed in 2013



isoprene

Carotenoids

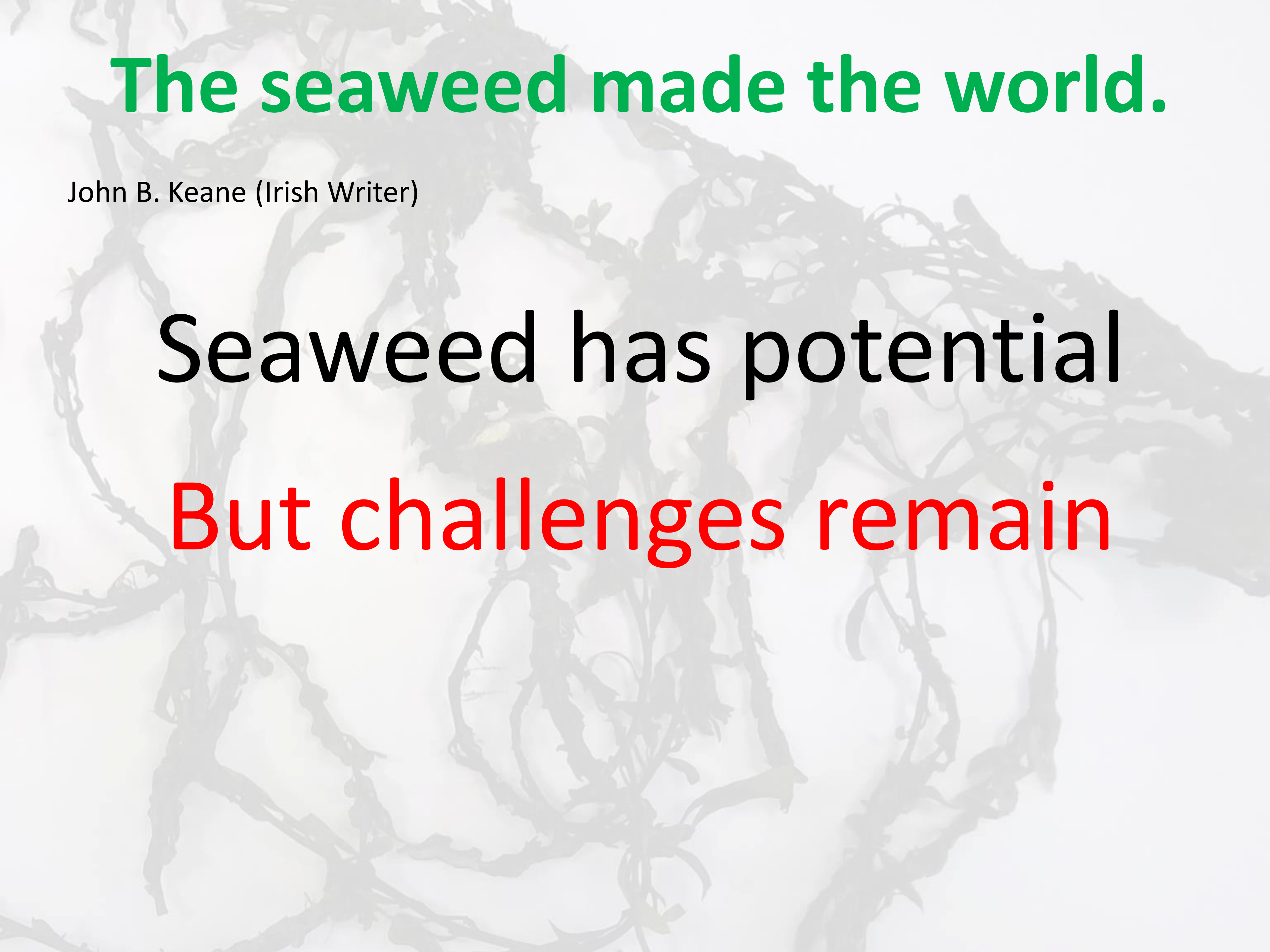
- Fucoxanthin

- antioxidant,
- anti-inflammatory
- anti-obesity,
- antitumor

Biorefinery

Fucoxanthin

€ 9000 g^{-1}



The seaweed made the world.

John B. Keane (Irish Writer)

Seaweed has potential

But challenges remain

Publications

- Milledge JJ, Harvey PJ (2016) Golden-tides: problem or golden opportunity? The valorisation of Sargassum from beach inundations J Marine Sci and Eng
- Milledge JJ, Harvey PJ (2016) Ensilage and anaerobic digestion of *Sargassum muticum* J Appl Phycol
- Milledge JJ, Harvey PJ (2016) Potential process ‘hurdles’ in the use of macroalgae as feedstock for biofuel production in the British Isles Journal of Chemical Technology & Biotechnology
- Milledge JJ, Nielsen BV, Bailey D (2015) High-value products from macroalgae: the potential uses of the invasive brown seaweed, *Sargassum muticum* Rev Environ Sci Biotechnol 15:67-88
- Milledge JJ, Staple A, Harvey P (2015) Slow Pyrolysis as a Method for the Destruction of Japanese Wireweed, *Sargassum muticum* Environment and Natural Resources Research 5:28-36
- Milledge JJ, Smith B, Dyer P, Harvey P (2014) Macroalgae-Derived Biofuel: A Review of Methods of Energy Extraction from Seaweed Biomass Energies 7:7194-7222

A large number of different sources of information have been used in this presentation. Citations for all the information can be found in the publications listed above.
Thank you to all those who have published data that is included in this presentation

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- Namibian Sun
- Kelly (Robinson) de Schaun

High Value Chemicals from Plants

EPSRC

IOTA Pharmaceuticals

University of Greenwich

Thank you