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Algal biochar – production and properties

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ABSTRACT

This study presents baseline data on the physiochemical properties and potential uses of macroalgal (seaweed) biochar produced by pyrolysis of eight species of green tide algae sourced from fresh, brackish and marine environments. All of the biochars produced are comparatively low in carbon content, surface area and cation exchange capacity, but high in pH, ash, nitrogen and extractable inorganic nutrients including P, K, Ca and Mg. The biochars are more similar in characteristics to those produced from poultry litter relative to those derived from ligno-cellulosic feedstocks. This means that, like poultry litter biochar, macroalgal biochar has properties that provide direct nutrient benefits to soils and thereby to crop productivity, and will be particularly useful for application on acidic soils. However, macroalgal biochars are volumetrically less able to provide the carbon sequestration benefits of the high carbon ligno-cellulosic biochars.

1. Introduction

Macroalgae (seaweeds) are ecologically and economically important, providing essential ecosystem services and biomass for foods, phycocolloids, soil additives, animal feeds and neutraceuticals (reviewed in Chopin and Sawhney, 2009). Selected commercial algal species are intensively cultured, mainly for use in the food and phycocolloid industries. Due to their rapid growth rates (Mata et al., 2010a), ability to assimilate nutrients such as nitrogen and phosphorous (Neori et al., 2003), and sequester (internally and externally) other elements such as heavy metals (Lobban and Harrison, 1994) they are also utilised for the bioremediation of waste waters, in particular from aquaculture systems (Barrington et al., 2009; Troell, 2009). Furthermore, because of high biological diversity across marine, brackish and freshwater systems, algae offer a robust solution to treating eutrophic (nitrogen- and phosphorous-rich) waters.

Consequently, these same characteristics often mean that some macroalgae become "pest" species in eutrophic environments (Lui et al., 2009; Pang et al., 2010) where they take advantage of anthropogenic nutrients, particularly in enclosed waters (Cohen and Fong, 2006; Pang et al., 2010). These fast growing, environmentally tolerant species are referred to as green tide algae because of their ability to rapidly colonise and dominate high nutrient environments (Raffaelli et al., 1998; Taylor et al., 2001; de Paula Silva et al., 2008; Nelson et al., 2008; Pang et al., 2010). Such algae are commonly members of the green algal genera *Cladophora*, *Chaetomorpha*, *Rhizoclonium*, and *Ulva*. The best example of this phenomenon was a recent macroalgal bloom of *Ulva prolifera* in the Yellow Sea, off China, with an estimated area of between 13,000 and 30,000 km^2 (Lui et al., 2009; Pang et al., 2010).

These same green tide algae species offer the advantage of being able to be cultured on non-arable land, and species can be selected to utilise water of almost any salinity and nutrient regime (Taylor et al., 2001; de Paula Silva et al., 2008; Nelson et al., 2008). This makes them an attractive solution for the sequestration of carbon through photosynthesis. Hence the production of algal biomass, from both microalgae and macroalgae, is proposed as a cost-effective solution for carbon sequestration and re-use. However, the implementation of macroalgal solutions for bioremediation and carbon sequestration is often restricted by the economic value of the potentially large quantities of biomass that can be generated. While microalgae are targeted as a source of lipids for algal oil including the production of biofuels (Chisti, 2007; Brennan and Owende, 2010; Mata et al., 2010b), macroalgae are lower in lipid content, and there is currently no obvious high-value end product for biomass from fast growing green tide species.

One potential end-use for algal biomass from green tide algae with high growth rates is the production of biochar. Biochar (charcoal) has demonstrated potential as a tool for carbon sequestration and as a soil ameliorant capable of improving water holding capacity and nutrient status of many soils (e.g. Lehmann et al., 2006; Lehmann and Joseph, 2009). Furthermore, the addition of biochar to many soils provides a substrate that supports enhanced microbial activity (Thies and Rillig, 2009).

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Macroalgae tend to be comparatively low in carbon but often high in nitrogen, phosphorus and other nutrients compared to many terrestrial biomass types (Ruperez, 2002; Ross et al., 2008). Therefore, it is reasonable to assume that biochar produced from algal feedstocks may also be comparatively high in nutrients including minerals. This may make algal biochar an attractive carbon sequestration and soil amelioration option, providing a high-value end product for macroalgal biomass. However, the proportion and composition of nutrients is likely to vary between species and from fresh, through brackish to saline environments.

As with other biochar feedstocks the potential also exists to produce power derived from the off-gases and/or oils produced during pyrolysis, and indeed, most research to date into potential uses for algal biomass, and microalgae in particular, has been directed toward energy generation (Ross et al., 2008; Brennan and Owende, 2010). Comparatively little research has been conducted into the suitability of algal biochar for carbon sequestration or soil fertility enhancement, though the potential in this regard has been noted previously for both macroalgae (Ross et al., 2008) and microalgae (Grierson et al., 2009).

A first critical step in assessing the utility of algal biochar for carbon sequestration and soil fertility enhancement is the quantification of the properties of algal biochar including a comparison with biochar produced from other commonly used terrestrial biomass feedstocks. This study therefore presents, for the first time, baseline information enabling an assessment of the physiochemical properties and potential uses of macroalgal biochar produced from eight species of green tide algae sourced from fresh, brackish and marine environments. Furthermore, this paper contributes to developing a value model for the production of green tide algae biomass for carbon sequestration, enhancing soil fertility, the bioremediation of waste water and the remediation of other anthropogenically impacted natural environments.

2. Methods

2.1. Study organisms, sample collection and stock cultures

Eight species of green tide filamentous algae were selected for the production and evaluation of biochar. All species were collected on the basis of ease of culture, use in bioremediation applications, and availability across a range of environments. The selected species were *Cladophora coelothrix* Kützing, *Cladophora patentiramea* (Montagne) Kützing, *Chaetomorpha indica* (Kützing) Kützing, *Chaetomorpha linum* (O.F. Müller) Kützing, *Cladophoropsis* sp., *Ulva flexuosa* Wulfen, *Cladophora vagabunda* (Linnaeus) Hoek. These are all related algae in the family Cladophoraceae and Ulvaceae (also see Table 1). The remaining species was *Caulerpa taxifolia* (M. Vahal) C. Agardh. Samples of all eight species were collected between March and August 2009.

The algal species *Cladophora coelothirx*, *Chaetomorpha indica* and *Chaetomorpha linum* were collected from Good Fortune Bay Fisheries Ltd. (Latitude: 20.02°S; Longitude: 148.22°E) (described in de Paula Silva et al., 2008). *Cladophora patentiramea* was collected at Pacific Reef Fisheries Pty Ltd. which is a land-based intensive tiger prawn (*Penaeus monodon*) farm located in Ayr (Latitude: 19.62°S; Longitude: 147.38°E). *U. flexuosa* was cultured at James Cook University – Townsville (Latitude: 19.33°S; Longitude: 146.76°E) as a nutrient scrubber for a large-scale (600,000 L) research recirculation system. *Caulerpa taxifolia* was also collected from James Cook University where it is cultured as a nutrient scrubber. *Cladophoropsis* sp. was collected by hand from the Reef HQ Aquarium System – Townsville. All species were sourced from saline marine waters (36‰). *Cladophora vagabunda* was collected from freshwater ponds at the Townsville Barramundi Fish Farm in Kelso, Townsville (Latitude: 19.36°S Longitude: 146.70°E).

Taxonomic identification of algae was based on Womersley (1984) and Kraft (2007). Algal taxonomic voucher specimens were preserved in 90% ethanol and lodged with the Herbarium of the Royal Botanic Gardens, Sydney, Australia. All algal samples for biochar production were unwashed, pressed dry and subsequently oven dried at 65 °C for 48 h for storage.

2.2. Initial selection of pyrolysis conditions

An initial experiment was conducted using *U. flexuosa* to compare the effect of pyrolysis temperature on the baseline physiochemical characteristics of algal biochar and to determine the batch-to-batch reproducibility of the pyrolysis process. The algal feedstock was initially dried to constant weight at 105 °C and a ~100 g aliquot was loaded into a wire mesh basket suspended in a sealed 2 L stainless steel vessel inside a muffle furnace. The stainless steel vessel was constantly purged with dry nitrogen gas at 3.5 L min^{-1} and the vessel heated over 30–40 min to a final hold temperature of 307 ± 5, 414 ± 5, 450 ± 5 or 512 ± 5 °C, monitored via thermocouple inserted directly into the centre of the sample. The final hold temperature was maintained for 60 min after which time the vessel was removed from the muffle furnace and cooled over ~20 min.

The algal biochar thus produced was immediately weighed and at least triplicate aliquots were produced at each temperature, indicating that weight loss accompanying pyrolysis in this manner is reproducible to better than ±3%. The biochar from all aliquots at each temperature were combined, mixed and lightly crushed by hand to pass 2 mm, 500 and 63 μm sieves, to provide >20 g of biochar in each fraction, sufficient for all analyses. A hold temperature of 450 ± 5 °C was found to provide a reasonable balance between efficient pyrolysis while minimizing mass loss during pyrolysis, and this temperature was chosen for all subsequent experiments using other algal species. All other experimental conditions were maintained as above.

2.3. Biochar characterization

Both the original dried algal feedstock and the algal biochar were subjected to a range of analyses in order to provide a basic

Table 1
Description and characteristics of algae used in this study. *Note*: Env. = environment of occurence, freshwater or saline; carb. = carbonate; LOI = loss on ignitions (at 550 or 1000 °C); ash = ash content; raw = unacidified samples analysed for C, H and N; acid = analysis of samples after acidification.

Species	Env.	Carb.	LOI 550 (%)	LOI 1000 (%)	Ash (%)	C raw (%)	N raw (%)	H raw (%)	C:N	C acid (%)	N acid (%)	H acid (%)
Cladophora coelothrix	Saline		75.2	14.2	10.5	32.1	4.0	4.1	8.0	31.4	3.7	4.8
Cladophora patentiramea	Saline		54.6	20.2	25.2	22.5	2.5	2.8	9.1	22.5	3.4	3.0
Chaetomorpha indica	Saline		48.0	41.2	10.8	20.6	3.0	2.9	7.0	20.5	4.5	3.2
Chaetomorpha linum	Saline		62.3	25.2	12.5	26.0	3.2	3.5	8.1	25.4	4.1	3.9
Cladophoropsis sp.	Saline	×	36.5	30.2	33.3	20.5	1.9	2.5	10.9	17.5	1.5	4.2
Caulerpa taxifolia	Saline		63.3	23.6	13.1	26.8	3.4	2.9	7.8	27.0	4.4	3.5
Cladophora vagabunda	Fresh	×	21.4	44.7	33.8	28.6	2.1	3.4	13.9	29.0	1.8	4.1

physio-chemical characterization of each raw and pyrolysed material. As the chemistry of individual macroalgal species, and therefore of biochar derived from macroalgae, has been shown to vary significantly both spatially and temporally (Ruperez, 2002; Marinho-Soriano et al., 2006; Renaud and Luong-Van, 2006), we used replicated analyses of *U. flexuosa* collected in March 2009 and August 2009 to provide a measure of the likely 'full' uncertainty associated with the analyses discussed below.

Carbon, nitrogen and hydrogen contents were determined by dry combustion using a Costech elemental analyser with routine analytical uncertainty better than ± 3% of the measured value. In addition, organic content was determined by loss on ignition at 550 °C for 2 h with carbonate content subsequently determined by ignition at 1000 °C for 1 h. As an additional check, carbonate content was also calculated from the difference in carbon content determined on untreated and acidified aliquots of each sample by elemental analysis.

Other analyses followed Australian standard methods for soil analysis, elucidated in detail in Rayment and Higginson (1992). Electrical conductivity and pH were determined in 10:1 water:biochar mixtures. Exchangeable bases (Ca, Mg, K, Na) and cation exchange capacity (CEC) were determined using Silver thiourea (AgTU) extracts, extractable phosphorus by Colwell bicarbonate extraction, total phosphorus by Kjeldahl digestion. Surface area was determined by nitrogen adsorption using standard techniques by Particle and Surface Sciences Pty Ltd., in Gosford, New South Wales, Australia.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were collected on powdered aliquots of each sample, from 400 to 4000 cm^{-1} at a resolution of 1 cm^{-1} using a Bruker Alpha-R spectrometer. Twenty-five scans per sample were averaged and baseline corrected and spectra analysed using Opus mentor software, and compared with published assignments for algae (Murdock and Wetzel, 2009).

3. Results and discussion

The physical and chemical characteristics of the algae are provided in Tables 1 (for all species other than *U. flexuosa*) and 2 (for *U. flexuosa*). All samples are comparatively low in carbon (20.5–32.1%), high in nitrogen (1.9–4.0%) with hydrogen contents ranging from 2.5% to 4.1%. The low carbon content, compared to ligno-cellulosic biomass, is typical of many macroalgae (e.g. Fernández-Aláez et al., 1999; Renaud and Luong-Van, 2006; Ross et al., 2008) and is due to a comparatively high ash content. The C:N ratio (7.0–13.9) is also typical of macroalgae. The ash content of the samples is difficult to measure as it was found that the ashing process at 550 °C pyrolysed a proportion of occluded organic carbon, leading to the product of the ashing process being dark grey to black in colour. Most of this occluded pyrolysed organic matter was ashed at 1000 °C but this led to an over-estimate of the carbonate content of the samples. The carbonate-free ash content of the samples ranged from 10.5% to 33.8%. Biogenic carbonate (indicated by fizzing of the sample in dilute acid) was confirmed in samples made from *Cladophoropsis* sp. and *Cladophora vagabunda*.

Table 2 details the results of detailed pyrolysis experiments on *U. flexuosa* collected at two different times to provide insights into the possible variability in algal feedstock chemistry and to determine optimal pyrolysis conditions. For most parameters measured on the raw algae, the results agree to within ±10% for the two different collections, with the exception of LOI at 1000 °C possibly due to more biogenic carbonate precipitation in the sample collected in August.

The loss of volatiles during pyrolysis increased slowly from 37% to 50% as temperature increased from 305 to 450 °C, then increased dramatically to 71% at 512 °C. The carbon, nitrogen and hydrogen content decreased as pyrolysis temperature increased, but there is little systematic variation in other parameters as temperature increased. Electrical conductivity (42–53 mS cm^{-1}), pH (8.0–10.1) and extractable phosphate (3647–4671 mg kg^{-1}) are all high compared to many terrestrial biomass biochars, while C:N ratio (5.8–8.4) remained similar to the ratio in the algae of 6.4. The cation exchange capacity of the biochars are relatively low (29–41 cmol(+) kg^{-1}) with extractable Ca, Mg and K ranging from 27 to 485 cmol(+) kg^{-1}. BET surface area was generally low for biochars produced at all temperatures, but did increase significantly with pyrolysis temperature, from 1.15 m^2g^{-1} at the lowest temperature to 4.26 m^2g^{-1} at the highest temperature.

FTIR indicated that there were changes in structure with pyrolysis temperature. A broad band at 3400 cm^{-1}, attributed to OH

Table 2
Average composition of *Ulva flexuousa* algae collected and processed separately in March and August 2009 and biochar derived from this alga under a range of pyrolysis temperatures. *Note*: "LOI" = loss on ignition; "CEC" = cation exchange capacity; "no acid" refers to raw samples, and "acid' to samples after acidification to remove carbonate.

Parameter	Units	Raw algae	Algal biochar			
Collection date (s)	Month	March and August	March	March	March and August	March
Pyrolysis temp (°C)	°C	N/A	305	414	450	512
Pyrolysis loss (%)	%	N/A	0.37	0.49	0.50	0.71
LOI @ 550 °C	%	63.5 ± 0.9	50.3	35.4	35.0 ± 2.8	30.1
LOI @ 1000 °C	%	17.1 ± 2.0	23.2	35.3	22.5 ± 3.7	38.9
Ash content	%	19.4 ± 1.7	26.5	29.2	42.6 ± 0.9	31.0
pH			8.0	9.8	10.0 ± 0.0	10.1
EC (mS/cm)	mS cm^{-1}		41.8	45.5	53 ± 2	51.8
BET surface area	m^2 g^{-1}		1.15	1.81		4.26
Carbon (no acid)	%	26.2 ± 1.7	28.9	25.7	22.6 ± 1.2	21.5
Nitrogen (no acid)	%	4.1 ± 0.3	5.0	3.9	2.7 ± 1	3.0
Hydrogen (no acid)	%	3.8 ± 0.3	2.8	1.9	1.2 ± 0.1	1.2
C:N ratio		6.4	5.8	6.6	8.4	7.2
Carbon (acid)	%	25.8 ± 1	30.9	24.5	24.2 ± 1.3	22.3
Nitrogen (acid)	%	6.0 ± 2.8	7.7	6.1	4.0 ± 1.2	4.9
Hydrogen (acid)	%	3.8 ± 1.2	3.2	2.3	1.6 ± 0.5	1.1
Extractable P	mg kg^{-1}		3647	4829	4671 ± 222	3211
Total P	mg kg^{-1}				7078 ± 877	
CEC	cmol(+) kg^{-1}		29	39	41 ± 1	36
Extractable Ca	cmol(+) kg^{-1}				27 ± 4	
Extractable Mg	cmol(+) kg^{-1}		125	180	104 ± 10	189
Extractable K	cmol(+) kg^{-1}		119	97	167 ± 24	69
Extractable Na	cmol(+) kg^{-1}				485 ± 26	

bonds, remained prominent at all pyrolysis temperatures. Distinct bands at 2965, 2930, and 2875 cm^{-1} are assigned methyl and methylene groups in fatty acids (Murdock and Wetzel, 2009). These lipid characteristic bands became more distinct at pyrolysis temperatures of 307 and 450 °C relative to untreated algae, but are absent at 512 °C. The prominent band at 1665 cm^{-1} is assigned to amide I (protein), and remained distinct at all pyrolysis temperatures. However, bands at 1550 cm^{-1}, assigned to amide II, are not present after pyrolysis at any temperatures investigated. A carboxyl diagnostic peak at 1430–1450 cm^{-1} is present on all spectra, but much reduced at 512 °C, while a peak from 1200 to 1100 cm^{-1} is attributed to polysaccharide rings and became most prominent at higher temperatures.

Based on the results for *U. flexuosa* (Table 2) a further seven algae were pyrolysed at 450 °C and the characteristics of these biochars are provided in Table 3. The biochars varied widely in composition, losing 20.9–54.2% of their original mass during pyrolysis, with ash contents ranging widely from 16.0 to 73.5%. Ash content was roughly negatively correlated with carbon (10.2–34.6%), nitrogen (1.1–3.3%) and hydrogen content (0.8–1.5%). C:N ratio after pyrolysis (9.4–11.1) increased in all cases relative to the raw algae, except the two cases where significant carbonate was present.

Cation exchange capacity was comparatively low in all cases, ranging from 16 to 23 cmol(+) kg^{-1}, while pH was alkaline, ranging from 7.8 to 10.1. Electrical conductivity was high (15.3–61.2 $mScm^{-1}$) for all biochars from saline species, but very low (2.8 mS/cm) for the sole freshwater species *Cladophora vagabunda*. The difference between freshwater and saline species was generally also apparent in the extractable cations, with extractable Na in saline species in the range 141–812 cmol(+) kg^{-1} while extractable Na was only 24 cmol(+) kg^{-1} in the freshwater species. The difference between fresh and saline species was not so marked in other extractable cations, which all lay in the range 11–475 cmol(+) kg^{-1}. Extractable P was uniformly high in all biochars, ranging from 914 to 2418 mg kg^{-1} and representing between 37% and 83% of the total P in the samples. BET surface areas determined for biochar from two species at 450 °C were low, as was the case with *U. flexuosa*, ranging from 4.33 m^2g^{-1} for *Cladophora coelothrix* to 5.73 m^2g^{-1} for *Cladophora vagabunda*.

FTIR spectra of the different species of algae at 450 °C were similar to the results for *U. flexuosa* at 450 °C, but did vary slightly in the sugar region, which we attribute to different abundances of cellulose. Prominent diagnostic $CaCO_3$ peaks were present in two specimens (*Cladophoropsis* sp. and *Cladophora vagabunda*). Despite these minor differences, all spectra after pyrolysis were similar except for notable $CaCO_3$ bands in these two species.

As presented above, the biochar derived from the macroalgal material used in this study displays a range of physical and chemical characteristics that are dependent on both pyrolysis conditions and original feedstock composition. The effect of pyrolysis temperature is most marked in terms of mass loss, which increases dramatically from 50% at 450 °C to 71% at 515 °C for *U. flexuosa*. Apart from resulting in a commensurate increase in ash content, pyrolysis temperature resulted in few other systematic changes in the chemical properties of the resultant biochar (Table 2). Therefore pyrolysis temperature is not a particularly critical variable, provided the temperature is higher than ~350 °C to ensure efficient pyrolysis (Ross et al., 2008), and lower than ~500 °C, to maximize biochar yield.

Comparison of the biochar produced from all eight species (Tables 2 and 3) indicates that there are many similarities in the properties of algal biochar, but some substantial differences. All of the biochars are comparatively low in carbon content, surface area and cation exchange capacity but high in pH, nitrogen and extractable inorganic nutrients including P, K, Ca and Mg. Poultry litter biochar made under similar conditions has been reported to have a carbon content of ~38%, nitrogen content of 2%, pH of 9.9, carbonate content of 15%, and an available P concentration of 11,600 mg kg^{-1} (Chan and Xu, 2009). Tagoe et al. (2008) produced biochar at 500 °C from poultry litter with 12.3% C, 2.6% N, pH of 9.93, and a P content of 18,170 $mgkg^{-1}$. In contrast, ligno-cellulosic biochar tends to have much higher carbon contents, and cation exchange capacities compared to the algal biochars, with pH values below 7 and significantly lower ash and available nutrient contents (Chan and Xu, 2009; DeLuca et al., 2009; Ozcimen and Ersoy-Mericboyu, 2010).

The algal biochars produced in this study are therefore similar to biochars produced from poultry litter, and dissimilar to biochars derived from ligno-cellulosic feedstocks. This means that, like poultry litter biochar, the algal biochars are likely to provide significant direct nutrient benefits to soils and crop productivity, and are likely to be particularly useful for application on acidic soils. However, they are volumetrically less able to provide the carbon sequestration benefits of the high-carbon ligno-cellulosic biochars.

Table 3
Characteristics of biochar produced from a range of algal species. *Note*: "LOI" = loss on ignition; "CEC" = cation exchange capacity; "no acid" refers to raw samples, and "acid' to samples after acidification to remove carbonate.

	Units	*Cladophora coelothrix*	*Cladophora patentiramea*	*Chaetomorpha indica*	*Chaetomorpha linum*	*Cladophoropsis* sp.	*Caulerpa taxifolia*	*Cladophora vagabunda*
Pyrolysis loss	%	50.2	37.3	24.8	43.4	44.2	22.9	42.9
LOI 550	%	48.5	32.0	16.6	34.3	15.0	36.2	28.1
LOI 1000	%	19.4	21.0	9.9	49.6	38.5	42.9	17.7
Ash	%	32.1	47.0	73.5	16.0	46.5	20.9	54.2
pH		8.72	9.12	7.83	9.61	10.07	9.65	9.87
EC	mS cm^{-1}	37.3	45.2	15.3	42.8	24.9	61.2	2.8
Carbon (no acid)	%	34.6	20.3	10.2	23.6	23.6	24.8	21.8
Nitrogen (no acid)	%	3.3	1.7	1.1	2.4	2.8	2.4	2.0
Hydrogen (no acid)	%	1.5	1.2	0.8	1.3	1.5	1.2	1.2
C:N ratio		10.4	12.2	9.4	10.0	8.5	10.4	11.1
Carbon (acid)	%	33.8	24.4	8.2	21.9	16.3	24.0	19.0
Nitrogen (acid)	%	5.3	2.8	1.6	3.3	2.7	1.8	3.2
Hydrogen (acid)	%	1.4	0.7	1.4	1.4	1.3	2.3	2.7
Extractable P	mg kg^{-1}	2418	973	914	2087	1265	1155	1413
Total P	mg kg^{-1}	5470	1712	1853	2515	2123	3089	3445
CEC	cmol(+) kg^{-1}	19	21	16	36	27	17	23
Extractable Ca	cmol(+) kg^{-1}	277	214	11	21	25	23	14
Extractable Mg	cmol(+) kg^{-1}	31	62	17	68	27	45	14
Extractable K	cmol(+) kg^{-1}	145	262	38	475	118	31	20
Extractable Na	cmol(+) kg^{-1}	288	331	141	318	152	812	24

The major differences among the algal biochars in this study are in their ash content, which is comparatively high in all cases but varies substantially between samples from 16% to 73.4%. Some particularly high ash contents are due to the presence of exogenous material (gastropods and sand) that could not be removed from some samples, most notably *Chaetomorpha indica*, *Cladophoropsis* sp. and *Cladophora vagabunda*. The high ash content of these samples directly affects their carbon and nitrogen contents, which are lower than the other samples and to a lesser degree lowers the concentration of available cations.

All the saline species have considerably higher electrical conductivities and extractable Na contents, relative to the single freshwater species (*Cladophora vagabunda*). The comparatively high salt content of the biochar derived from the saline species could potentially be an issue for the use of saline algal biochar as a soil ameliorant. However, many current inorganic fertilizers contain nutrients in the form of salts (potassium chloride and ammonium sulphate for example) and these are widely in use without detrimental effect, providing the soils are relatively well drained.

The intensive culture of macroalgae provides opportunities to remediate nitrogen and carbon wastes through biomitigation. The broad spectrum of environmental tolerance of green tide species, their rapid growth rates and ability to be cultured through fragmentation make them ideal candidates to sequester carbon, nitrogen and phosphorus from the environment. One of the most effective strategies for the application of green tide algae is through integration with pond-based aquaculture, or land-based agriculture, which can support extremely high growth rates through the provision of nutrients and carbon dioxide (Neori et al., 2003, Mata et al., 2010a).

Integrated aquaculture-agriculture systems, whereby the nutrient effluent from aquaculture-agriculture production is used as a nutrient source for further production of animals, crops or biomass, is increasingly seen as a tool for reducing environmental damage and increasing aggregate production from agriculture (Craggs et al., 1996; Prein, 2002) and aquaculture (Barrington et al., 2009; Chopin and Sawhney, 2009; Troell, 2009). However, one of the major limitations in implementing these systems is a viable market for the end-product of macroalgal biomass. The use of macroalgal biomass for biochar production, with energy co-generation potential offers a commercial solution to "pull" the implementation of integrated aquaculture-agriculture systems. The results from this study suggest that algal biochar derived from remediation of aquaculture wastewater, and indeed from algal biomass in eutrophied natural water bodies, will be suitable as both a soil ameliorant and as a tool for increasing soil carbon sequestration potential.

In Australia, 30% of aquaculture pond area must be used for wastewater remediation, amounting to approximately ~15 Ha for an average aquaculture operation. Macroalgae productivity in integrated systems has a maximum exceeding 100 g (dry weight) $m^{-2}day^{-1}$ (Mata et al., 2010a). However, conservative pond-based systems with green tide algae can operate at 20 g (dry weight) $m^{-2}day^{-1}$ (estimated from de Paula Silva et al., 2008). This would produce 200 kg Ha^{-1} day^{-1}, 1.4 t Ha^{-1} $week^{-1}$ or 72.8 t Ha^{-1} $year^{-1}$. Therefore an average aquaculture operation with 15 Ha of bioremediation could produce 1092 t of dry algal biomass per year. If this were totally utilised for biochar production, such an operation could produce approximately 500 t per year of biochar. Assuming a minimal USD $400 per tonne value as fertilizer (noting biochar is being sold at up to USD $700 per tonne), this biochar would have a value of USD $200,000 per annum. Using the average carbon content for the algal biochar produced for this study of ~23%, the carbon sequestration potential for an average-sized aquaculture operation in Australia would be equivalent to ~500 t CO_2-e per annum. The co-generation of energy during the manufacture of biochar would generate a further income stream, and additional savings in greenhouse gas emissions.

China is the single largest aquaculture producer with over five million hectares of inland aquaculture operations in 2003. While environmental protection in China lags that in Australia, even partial implementation of a similar regime to Australia in the future could yield substantial carbon sequestration benefits in the range of high tens to low hundreds of megatonnes CO_2-e per annum.

Finally, similar calculations can be applied for industries that require the mitigation of carbon through biological carbon capture and storage, such as coal fired power stations, or the productive use of large co-generated waste water streams such as coal seam gas production. Algal biochar provides a value-driven model to sequester carbon, nitrogen and phosphorous, while utilising abundant non-potable (saline) water sources on non-arable land.

4. Conclusions

This study has demonstrated that biochar derived from macroalgae has properties likely to make it suitable for use both as a soil ameliorant and as a tool for long-term carbon sequestration. Algal biochar, derived from the remediation of wastewater from aquaculture, agriculture, eutrophied natural waterways, or saline waste water sources could provide a significant revenue stream in the future through energy co-generation, carbon credits from providing long-term soil carbon sequestration, and sale as a soil ameliorant and fertilizer. Further studies are underway to test the impact of algal biochar on soil properties and plant productivity.

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